First-Principles Determination of Giant Adsorption-Induced Surface Relaxation in $p(1\times1)$ O/Fe(001)

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We report results from a first-principles total-energy study of primitive (1×1) O chemisorbed on magnetic Fe(001). The adsorption-induced relaxation is found to be a factor of 3 larger than was inferred earlier from an analysis of LEED intensity data, reflecting strong covalent O-Fe bonding. The resulting arrangement of surface Fe and O atoms already closely resembles a rocksalt FeO monolayer which is comparatively weakly bound to the substrate. The surface bands are compared with angle-resolved photoemission data of Panzner, Mueller, and Rhodin.

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Though gaseous chemisorption on metallic surfaces is known to induce outward surface relaxations, very little is understood about the origin and nature of this effect and its impact on electronic and magnetic structure. In the case of oxygen chemisorbed on Fe(001), which may be an important precursor of the oxidation of Fe surfaces, not only is surprisingly little known about the associated adsorption-induced relaxation of the Fe surface [Fe/(*S*)] layer, only limited information is available about this particular adsorption.

Disagreement has existed within the last five years concerning even such a fundamental question as whether or not specific ordered O/Fe chemisorption phases occur.[1-4] For the one phase which has been consistently observed, primitive 1×1 [$p(1\times1)$] O on Fe/(001), non-spin-polarized, angle-resolved, ultraviolet photoemission experiments by Panzner, Mueller, and Rhodin[5] provide the only measurements of the adsorbate-induced, surface-state spectrum. Huang and Hermanson[6] have performed the only *ab initio* calculation of the electronic and magnetic structure of $p(1\times1)$ O/Fe(001), but these authors did not attempt to determine the associated relaxation or adsorbate height. In the handful of first-principles studies of gaseous chemisorption in which some attempt has been made to determine the adsorbate-surface geometry[7,8] from the minimum of the total energy, none has incorporated the possibility of surface relaxation.

In this Letter we report the first first-principles determination of an adsorption-induced surface relaxation, which includes the determination of the positions of *both* the surface and adsorbate from the minimum of the local-density total energy. The results indicate that for $p(1\times1)$ O/Fe(001), the outward relaxation of the Fe(*S*) layer is a factor of 3 larger than the value which was inferred earlier by Legg, Jona, Jepsen, and Marcus[3] (henceforth, LJJM) from the analysis of LEED intensity data. However, LJJM only considered a small range of Fe relaxations. We also find evidence for considerable covalence, including an adsorption-induced enhancement of the magnetism in the Fe(*S*) layer as well as a $0.2\mu_B$ moment on the oxygen atom. This is also reflected in a surprising sensitivity of the adsorption-induced change in work function $\Delta\phi$ with respect to variation of the adsorbate and surface positions. The agreement of our calculated value for $\Delta\phi$ with experiment is considerably better when the relaxation is accounted for correctly than when (1) the geometry inferred by LJJM is assumed, or (2) the Fe(*S*) is placed either at the position predicted by LJJM or near its location in an idealized bulklike film while the oxygen position is determined from the minimum of the total energy.

We have determined the equilibrium geometry of $p(1\times1)$ O/Fe(001) using the full-potential linearized augmented plane-wave (FLAPW) method.[9-11] We have used a seven-layer Fe slab with and without an additional $p(1\times1)$ O monolayer on each surface, with the O atoms placed in the fourfold hollows.[12] The amount of Fe(*S*) relaxation and the height of the oxygen were determined by evaluation of the total energy for eighteen different arrangements of the surface and adsorbate layers, with the positions of the remaining Fe layers held in fixed bulklike positions. Five additional studies served as checks of a different sampling (through multiple energy windows) of the variational freedom of the basis set. A significant savings in computational resources was made possible during this massive series of calculations by our use of a newly developed film-FLAPW Broyden technique, which we adapted from the existing bulk procedure[13] for determining self-consistent solutions of the Kohn-Sham equations.

The total-energy results are summarized in Fig. 1. Figure 1(a) shows the total energy per surface-region unit cell (one-half the total energy per film unit cell) as the Fe(*S*) position varies, with the O positioned at the calculated equilibrium height $d_O[\text{eq}]=0.71$ Å relative to the ideal, unrelaxed surface. Figure 1(b) shows the total energy per surface region as the oxygen height is varied for the indicated positions of the Fe(*S*) layer. These data allow us to make the first estimate, 71 ± 10 meV, of

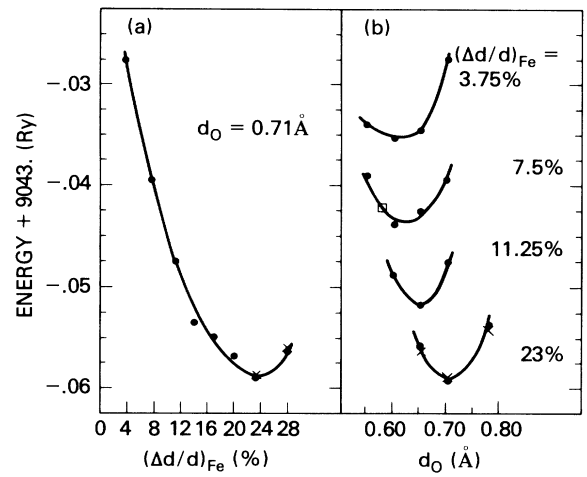

FIG. 1. (a) Total energy per surface-region unit cell=one-half the total energy per film unit cell as a function of change $\Delta d_{\rm Fe}$ of the Fe surface layer position, expressed relative to the Fe spacing $d_{\rm Fe}=2.70845$ a.u., with the O positioned at the equilibrium height. The minimum occurs at $(\Delta d/d)_{\rm Fe}=23\%$. (b) Total energies per surface-region unit cell vs the oxygen position relative to the position of unrelaxed Fe(S) layer. Results are shown for four values of $(\Delta d/d)_{\rm Fe}$. In both panels, crosses mark the total energies of two-window calculations (in which O 2s states are treated as semicore), shifted by the constant value of +14.5 mRy. The square marks the interpolated value of the energy for the geometry predicted by LJJM.

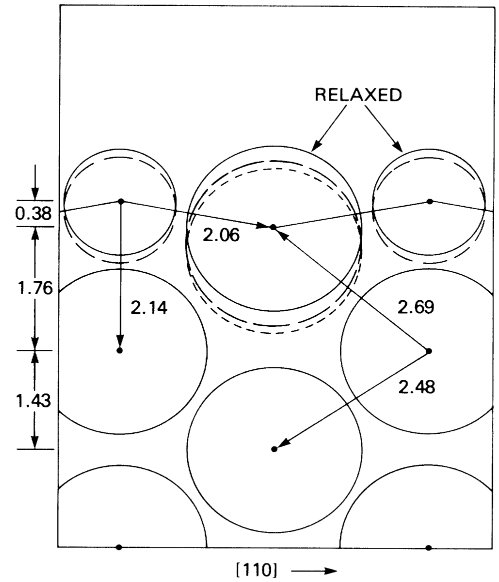

FIG. 2. The geometry predicted by the current work (dots), and the resulting bond-length predictions (in angstroms). Large (small) circles represent Fe (O) atoms. The orientation predicted by LJJM (Fig. 10 of Ref. 8) is shown by the long-dashed circles. The shorter-dashed circles mark the position of the unrelaxed Fe(S) atom.

the perpendicular vibrational energy of the O and also reveal that this quantity is relatively insensitive to variations of $d_{\rm Fe}$. The square in Fig. 1(b) marks the interpolated total energy for the geometry proposed by LJJM ($\Delta d/d_{\rm Fe}=7.5\%$, $d_{\rm O}=0.59$ Å), which is 17 mRy above the calculated minimum.

Figure 2 shows the calculated geometry as well as that predicted by LJJM. The predicted Fe surface relaxation, $\Delta d_{\rm Fe}=0.33$ Å, is 23% of the Fe interlayer spacing and is *3 times greater* than was inferred by LJJM from an analysis of LEED intensity data.[3] Important distinctions between the two geometries can be understood from the associated shifts in bond lengths and the orientation of the O relative to atoms in *both* the Fe(S) and Fe($S-1$) layers. The equilibrium geometry leads to an increase by 8.5% in the Fe(S)-Fe($S-1$) bond length, reflecting a considerable weakening of this bond. LJJM predicted a comparable increase of 2.7%. We find that the O-Fe(S) bond length is 0.08 Å shorter than the O-Fe($S-1$) separation. Because the resulting O-Fe(S), O-Fe($S-1$), and Fe(S)-Fe($S-1$) bond lengths are all within ~3% of the comparable spacings in bulk FeO,[14] our result implies a surface atomic structure closely resembling a strongly bound *planar* rocksalt FeO monolayer which is comparatively weakly bound to the substrate. Because of the large relaxation and similarly to FeO, we speculate that this behavior is relevant to the complex problem of the oxidation of Fe surfaces.

For both the FLAPW and LJJM predicted geometries, the chemisorption leads to the same increase in charge, 0.47e, in essentially the same proportion as that of majority to minority spins (0.33/0.14) on the O. This induces a small moment ($0.2\mu_{\rm B}$) for both geometries. The rather small size of this increase and the closeness of the adsorbate to the surface [0.38 (0.45) Å for the 23% (7.5%) relaxation case] lead to the formation of a small dipole layer, which accounts for the resulting smallness of the increase in $\Delta\phi$, 0.65 (0.95) eV. The smaller value, $\Delta\phi=0.65$ eV, at our calculated equilibrium, which is in considerably better agreement with experiment ($\Delta\phi \lesssim 0.4$ eV),[2,4,15] results largely as a consequence of the smaller increase in charge (0.07e vs 0.14e) in the Fe(S) atom. Also, however, the greater O-Fe($S-1$) and Fe(S)-Fe($S-1$) bond lengths in the 23% case lead to a narrowing and localization of the surface and subsurface d bands and core and a delocalization of the associated sp electrons through hybridization. This further reduces the dipole and leads to an upward shift of the local electrostatic potential. Because of the large exchange splitting in iron, this upward shift leads to a significant loss of minority electrons relative to the 7.5% case, especially in the Fe($S-1$) atom. As a consequence, surprisingly large enhancements (by ~10%–15%) in the magnetic moments[16] are induced on both the Fe($S-1$) and Fe(S) atoms. Even in the 7.5% case, there is an enhancement (by ~10%) of the moments of these atoms.

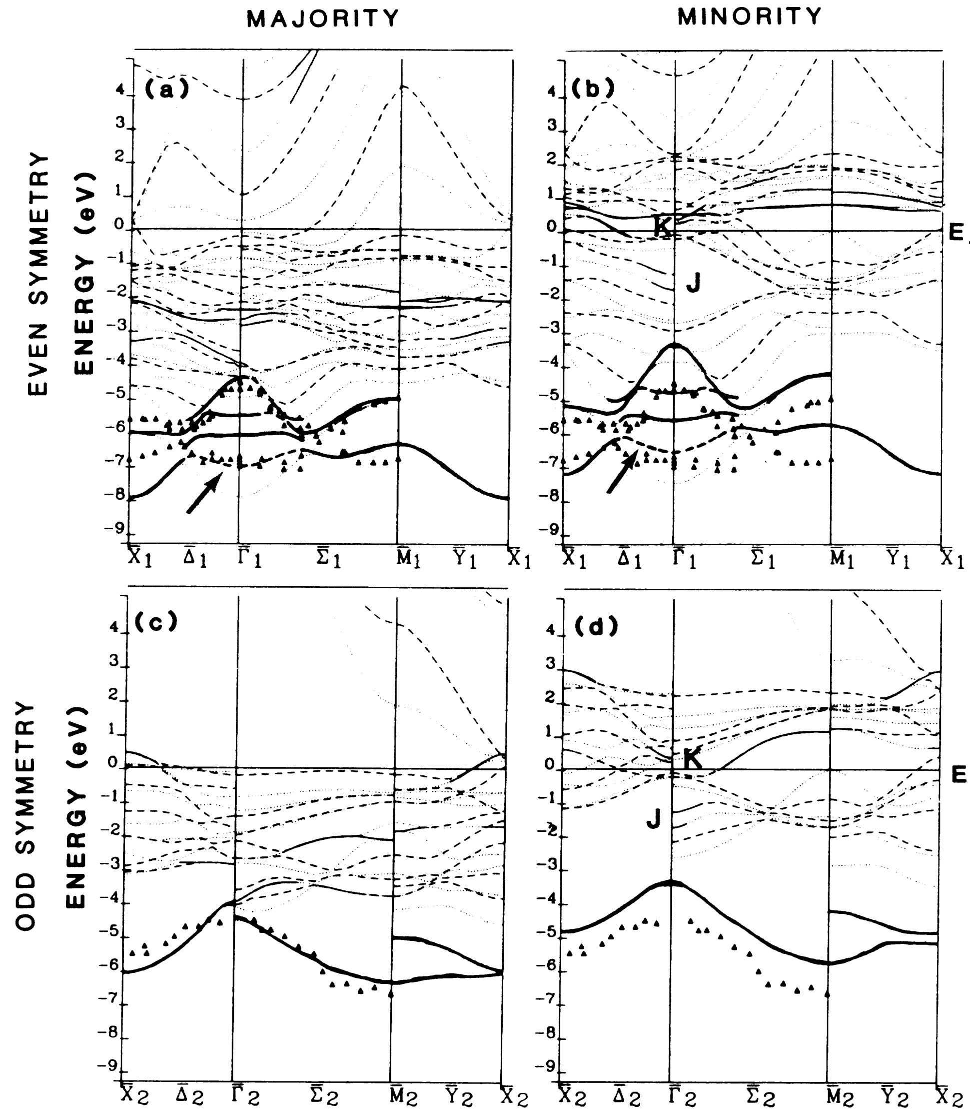

FIG. 3. Calculated equilibrium-band structures, resolved by spin and k-reflection symmetry. Symmetric (antisymmetric) states with respect to z reflection are shown by dotted (dashed) lines. Bold solid lines mark surface states of predominantly O-Fe(S) character; thinner solid lines designate Fe(S)-like states. Bold dashed lines above the arrows in (a) and (b) designate bands of O-Fe($S-1$) character. Triangles mark the positions of the non-spin-polarized ARPES measurements of energy bands by Panzner, Mueller, and Rhodin (Ref. 5). The letters J and K in (b) and (d) are used to indicate positions of the relaxation-sensitive, minority surface resonances, as discussed in the text.

The considerably greater loss of minority states for the 23% case in the Fe($S-1$) and Fe(S) layers leads to clearly distinguishable adsorption-induced changes in the hyperfine fields [$\Delta B_{\rm hf}=B_{\rm hf}(\rm O/Fe)-B_{\rm hf}(\rm Fe)$] for the two geometries. In particular, for the LJJM orientation, we find $\Delta B_{\rm hf}(\mathrm{Fe}(S-1))=+25$ kG and $\Delta B_{\rm hf}(\mathrm{Fe}(S))=-47$ kG; the corresponding values for the equilibrium geometry are -4 and 0 kG. *In situ* Mössbauer experiments could be used as a means of verifying our prediction[16] of a negligible change in $B_{\rm hf}(\mathrm{Fe}(S))$.

In Fig. 3, we have plotted the band structures, surface states, and surface-resonance states for our predicted equilibrium geometry, resolved by spin, symmetry with respect to reflection through the plane of the wave vector, and z-reflection symmetry. We have also included the experimental data derived by Panzner, Mueller, and Rhodin[5] from non-spin-polarized, angle-resolved photoemission spectroscopy (ARPES) measurements.

The most important distinctions in our band structures for the LJJM and equilibrium geometries occur in bands above -4 eV (all energies are referenced to $E_F=0$). Specifically, in the minority states, at $\bar{\Gamma}$ with energy

~ -1.5 eV, a new Fe(S) relaxation-induced surface resonance is induced, marked by J in Figs. 3(b) and 3(d), which is $d(x^2-y^2)$-like. We find a second, clearer example of a relaxation-induced Fe(S) resonance, labeled K, in the unoccupied spectrum at $\bar{\Gamma}$ with energy ~ 0.3 eV. The existence of both resonance states provides an important internal consistency check of the calculation because they are sensitive to the relaxation and are not identifiable as resonances at the LJJM orientation. These are the first predictions, to our knowledge, of relaxation-induced surface-resonance states on a transition metal arising entirely through an adsorption-induced relaxation. Additional, important, relaxation-induced features occur at $\bar{M}$, which are discussed elsewhere.[17]

In the -3- to -7-eV region, where ARPES measurements[5] of the spectrum have been made, our calculated bands for both the equilibrium and LJJM geometries are very similar and also closely resemble those reported by Huang and Hermanson,[6] derived from a five-layer film with the LJJM geometry. Also, in this region, Fig. 3 shows quite clearly the close agreement of experiment with the calculated *majority bands,* whereas the large exchange splitting of these states results in our calculated minority surface bands being shifted ~ 1 eV above the experimental data points. This finding suggests that the electron emission in these non-spin-polarized experiments originates from oxygen-derived surface bands of predominantly majority character. A possible reason for this is that considerable minority-majority splitting of these bands occurs; as a consequence, the associated minority states extend well into the majority d bands, which may have inhibited observation of the associated minority component. Also, considerably greater Fe character is present in the majority surface states. Thus, the initial majority and minority states are very different, which could give rise to a preselection of majority states in the ARPES experiment. It is also possible that antiferromagnetic ordering could occur similar to FeO which would complicate the interpretation of the experimental data. Clearly, spin-resolved experiments would help resolve this puzzle.

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