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Metal-Surface Reconstruction Induced by Adsorbate: Fe(110)$p(2\times2)$-S

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Reconstruction of the Fe(110) surface by a quarter monolayer of S is shown by low-energy electron-diffraction intensity analysis to correspond to a model in which hard-sphere atoms displace to a unique jamming point. After reconstruction the S atoms sit in fourfold hollows of touching Fe atoms with S-Fe bond lengths of 2.17 and 2.36 Å. A general construction for 2×2 reconstructions with rectangular symmetry is given and applied to this case and to Ni(001)(2×2)-C.

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Clean metal surfaces generally do not reconstruct, i.e., rearrange the atoms of the surface layers to give a different unit cell than the bulk.[1] However, when the surface has an ordered adsorbate with a different unit cell than the substrate bulk, reconstruction of the top substrate layers to the adsorbate unit cell and symmetry[2] should be universal. The atom displacements from bulk positions are small for the low-index (high-packing-density) surfaces commonly studied, since the range of movement is limited by the jamming of atoms against each other. A successful quantitative study has previously been carried out for only one case, Ni(001)(2×2)-C by low-energy electron-diffraction (LEED) intensity analysis.[3] We report here the case of Fe(110)$p(2\times2)$-S also studied by LEED intensity analysis, which resembles the Ni case, but shows interesting differences. In both cases an adsorbate atom is situated in a fourfold hollow site of the metal surface, i.e., a hollow surrounded by four atoms, not necessarily at the same distance, and the presence of the adsorbate induces a 2×2 reconstruction which enlarges that hollow by contracting other hollows. However, in the Fe case there is rectangular symmetry and the reconstruction is induced by a quarter monolayer of S atoms, whereas in the Ni case the structure retains fourfold rotational (but not square) symmetry and is induced by a half monolayer of C atoms. In the Fe case, the analysis shows that both adsorbate and reconstructed substrate have 2×2 symmetry, hence an intensity analysis is required to determine that the Fe atoms have moved from their bulk positions; in the Ni case, the adsorbate has $c(2\times2)$ symmetry and the presence of additional diffracted beams indicates directly that the substrate has a $p(2\times2)$ reconstruction. The anisotropy of the Fe case suggests a simple mechanism in which the S atom increases the two shorter bonds and shortens the two longer bonds to its surrounding four atoms until the displaced atoms jam (as fixed by bulk hard-sphere radii); the mechanism in the Ni case is not as clear and the reconstruction appears to stop 70% of the way to jamming. The fit of the theory to experiment in the Fe case is of good quality, comparable to the better analyses of adsorbate systems which are not complicated by significant substrate reconstruction[4]; the fit in the Ni case is only fair, leaving some uncertainty in the magnitudes of substrate movement.

The experiment on Fe(110) used an ultrahigh-purity Fe(110) specimen provided by the American Iron and Steel Institute. *In situ* cleaing procedures and a satisfactory LEED intensity analysis of clean Fe(110) have been reported.[5] Sulfur atoms were deposited at 10^{-10} Torr from a break-off capsule with use of gentle heating. The LEED patterns showed that the initial 1×1 structure of clean Fe(110) changed first into a $p(2\times 2)$ and then into a "quasi $\sqrt{3}$"[6] structure. Both LEED patterns were comparable in quality to that of the clean surface and among the best we have ever observed. Auger-electron spectroscopy was used to monitor the surface chemical composition. Previous work on Fe(001) of similar character[4] suggested that both structures were submonolayer coverages and the present analysis confirms that the $p(2\times 2)$ structure corresponds to a $\frac{1}{4}$ monolayer. Two sets of spectra were collected: eight beams at normal incidence and seven at $\theta = 9°$, $\varphi = 35.26°$. These spectra were corrected for background and for contact-potential difference (3.7 eV), and normalized to constant incident current. The calculations used eight phase shifts and 124 beams, the potentials employed successfully in previous studies of clean Fe and S on Fe surfaces,[4,5] a complex inner potential of $-(11.5+4.0i)$ eV (independent of energy), and a thermal vibration amplitude of 0.115 Å.

Fitting the LEED data was carried out in a two-stage process which first introduced a simple model (Model I) to test the fit without reconstruction and to evaluate the Fe-S interlayer distance d_z. The second stage used d_z and a hard-sphere model of reconstruction to find Model II, which was then verified. Model I put the S atoms in the fourfold hollows of the Fe(110) surface and left all Fe atoms in bulk positions (Fig. 1). Model I gave moderate agreement with measured curves at an S-Fe interlayer distance $d_z = 1.43$ Å but showed several discrepancies (see Fig. 2). Several other models were tried and rejected [in-

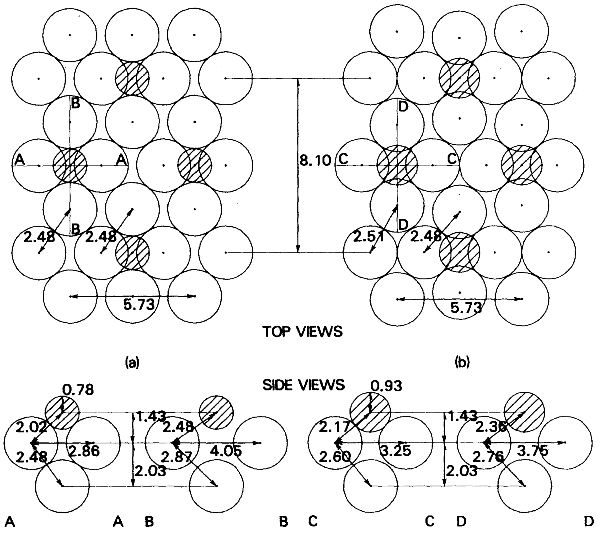

FIG. 1. Models of top substrate and adsorbate layers Fe(110)(2×2)-S, S atoms shaded, Fe atoms clear, distances in Å. (a) Model I: unreconstructed substrate, $d_1/d = d_3/d = 1.1547$, and $d_2/d = d_4/d = 1.6330$. *AA* and *BB* indicate lines along which side view is shown. (b) Model II: reconstructed substrate, $d_1/d = 1.0000$, $d_2/d = 1.7542$, $d_3/d = 1.3094$, and $d_4/d = 1.5118$.

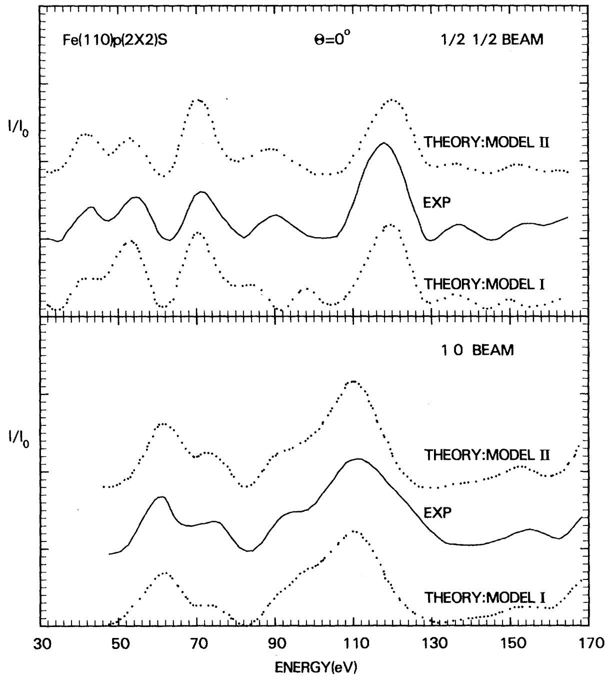

FIG. 2. Experimental LEED spectra (solid lines) and theoretical spectra (dotted lines) for Model I (simple overlayer) and Model II (reconstructed substrate with overlayer) of Fe(110)(2×2)-S.

cluding the quasi-threefold position which has been proposed[7] for adsorption on another bcc (110) surface, namely W(110)$p(2\times1)$-O]. A clue to an adequate model came from comparison of the S-Fe bond length of 2.02 Å in Model I with the 2.30 Å found[5] for S on Fe(001) and comparison with the (estimated) bond length in the diatomic molecule of 1.99 Å.[8] Both these comparisons suggested that the bond length of Model I was too short. The bond length could only be increased while preserving $d_z = 1.43$ Å (which should be relatively insensitive to parallel displacements of the Fe atoms) by enlarging the fourfold hollow. Such enlargements can be produced by a reconstruction which rearranges hard spheres with the bulk radius into 2×2 cells while preserving the rectangular symmetry and the commensurability with the substrate bulk. Figure 3 shows a general construction for such a rearrangement based on alternating rhombuses of types I and II with diagonals d_1, d_2, d_3, and d_4 as indicated. The condition for a 2×2 structure on the bcc (110) surface requires $d_1 + d_3 = 2.3094d$, $d_2 + d_4 = 3.2660d$, where d is the hard-sphere diameter. The conditions $d_1, d_2, d_3, d_4 \geq d$, $(d_1^2 + d_2^2)$, $(d_3^2 + d_4^2) \geq 4d^2$ eliminate possible overlaps. The allowed ranges of d_1 and d_2 for both bcc (110) and fcc (001) surfaces are shown in Figs. 4(a) and 4(b). Model II is the point A in Fig. 4(a) along the line $d_1 = d$ which corresponds to jamming of two atoms and is the point in the allowed region which makes the hollow in the type-II rhombus most nearly square ($d_4/d_3 = 1.15$ compared with 1.41 for Model I and 1.00 for a square). The atom arrangements and bond distances for both Models I and II are shown in Fig. 1 and the improved agreement of the calculated LEED spectra for Model II is shown in Fig. 2. The best fit for Model II is obtained with the same $d_z = 1.43$ Å and with the first interlayer spacing between Fe layers within 0.05

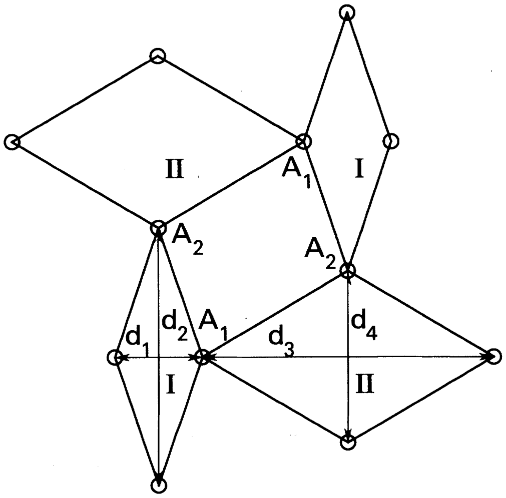

FIG. 3. General construction for finding rectangular 2×2 reconstructions of layers of hard spheres by alternating sequences of rhombuses of types I and II. Type I has diameters d_1 and d_2; type II has d_3 and d_4. The corner atoms A_1 and A_2 show the two types of local environment.

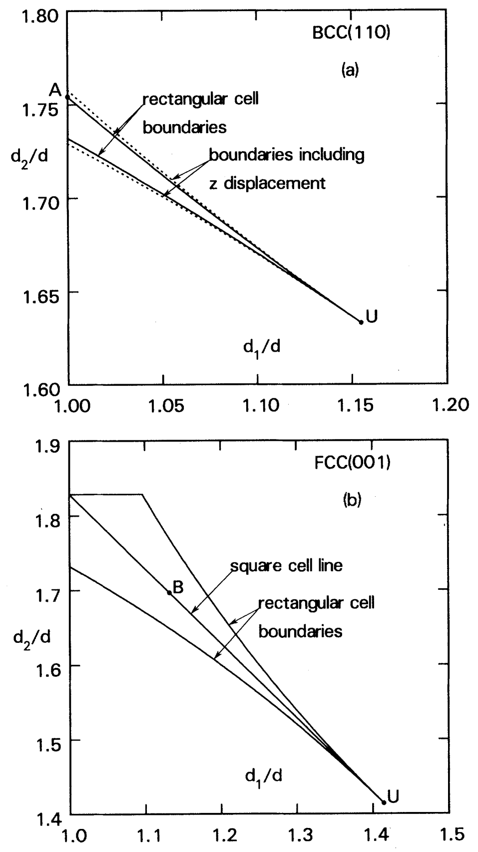

FIG. 4. Two examples of allowed regions on the d_1/d and d_2/d plane for rectangular 2×2 reconstruction of layers of hard spheres with bulk diameter d. The allowed regions are bounded by two marked boundary curves and a vertical and [in 4(b)] horizontal line. A symmetrical allowed region exists in which d_1/d increases and d_2/d decreases from the point U marking the unreconstructed surface. (a) bcc (110) surface, packing density 0.8330. Point A gives the most nearly square fourfold hollow of type II. Dotted line shows the boundaries when the z coordinates of the first-layer hard spheres change as the spheres roll on the second layer. (b) fcc (001) surface, packing density 0.7854; note change of scale from (a). Point B on the line along which the lattice retains fourfold symmetry is the point found in Ref. 3 for Ni(001)(2×2)-C.

Å of the bulk value. The point B in Fig. 4(b) on the line corresponding to square unit cell in the reconstruction of fcc (001) marks the position found[3] for Ni(100)(2 × 2)-C.

We note that to obtain Model II from Model I, the type-A_1 Fe atoms (Fig. 3) move 0.20 Å along d_1 while type-A_2 atoms move 0.12 Å along d_2. Model II also implies displacements perpendicular to the surface as the atoms ride upon the layer beneath, held in bulk positions, and are 0.12 Å for type-A_1 atoms and -0.03 Å for type-A_2 atoms, producing a buckling. The LEED calculations ignore the buckling and use an average displacement for the S plane. The perpendicular displacements slightly affect the jamming limits, shown by the dashed curve in Fig. 4(a), but were not used in fixing the parameters of Model II. The S-Fe bond lengths to nearest neighbors are now increased to 2.17 Å [Fig. 1(b)] and the bond length to next-nearest neighbors has shortened to 2.36 Å.

We conclude, therefore, that this system provides a clearcut illustration of reconstruction driven by adsorbate bonding forces. These forces take advantage of the greater freedom of motion of surface atoms to position the substrate atoms at the most favorable bond lengths, limited only by jamming. We are thus led to a unique selection out of a two-parameter set of possible reconstructions based on a model of hard (nonoverlapping) spheres with the bulk radius; all reconstructions retain rectangular symmetry and form 2 × 2 cells commensurate with the substrate. This unique model could then be verified by LEED intensity analysis, which fixes S-Fe bond lengths that closely bracket the bond lengths previously found for S on Fe(001).

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[1] The seven metals Au, Pt, Ir, V, Cr, Mo, and W are known to reconstruct on various faces. More will undoubtedly be found as more-open surfaces and new methods of preparation are studied. Almost all metal surfaces show a contraction of the first interlayer spacing.

[2] The reconstruction cell can be larger than but still commensurate with the adsorbate cell, as in the Ni(001) case discussed by Julia H. Onuferko, D. P. Woodruff, and B. W. Holland, Surf. Sci. 87, 357 (1979).

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[4] For example, Fe(001)c(2× 2)-S, where S sits in fourfold hollows with square symmetry, but the substrate does not reconstruct: K. O. Legg, F. Jona, D. W. Jepsen, and P. M. Marcus, Surf. Sci. 66, 25 (1977).

[5] H. D. Shih, F. Jona, V. Bardi, and P. M. Marcus, J. Phys. C 13, 3801 (1980).

[6] The vector definition of the quasi $\sqrt{3}$ structure is $\vec{a}_s = 2\vec{a} + \vec{b}$ and $\vec{b}_s = -\vec{a} + \vec{b}$, where $\vec{a}_s$ and $\vec{b}_s$ are the basic vectors that define the surface net, and $\vec{a}$ and $\vec{b}$ are the basic vectors of the substrate net, which define a primitive (rhombic) unit mesh with an angle of 109.47° between $\vec{a}$ and $\vec{b}$.

[7] M. A. Van Hove and S. Y. Tong, J. Vac. Sci. Technol. 12, 230 (1975).

[8] The Fe-S bond length in FeS crystal, with coordination number 6, is 2.45 Å. The bond length of the diatomic molecule is usually substantially less than the adsorbed-atom bond length, e.g., FeO (diatomic) = 1.57 Å, FeO (adsorbed) = 2.02 Å. No values for FeS (diatomic) have been found in the literature, but an estimate can be made by comparing bond lengths of diatomic oxides and sulfides of the same element in cases where both have been measured. The mean difference can then be combined with the Fe-O diatomic bond length for the estimate. Twenty-one such cases are listed in *Molecular Spectra and Molecular Structure IV: Constants of Diatomic Molecules*, edited by K. P. Huber and G. Herzberg (Van Nostrand Reinhold, New York, 1979): For example, CuO, 1.72 Å; CuS, 2.05 Å; MgO, 1.75 Å; MgS, 2.14 Å; etc. The mean value and standard deviation of the differences are 0.42 and 0.06 Å, which suggests a value for FeS of 1.99 ± 0.03 Å at the 95% confidence level on using the t test for samples of size 21 from a normal parent distribution.