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Early stages of oxidation of the Fe{001} surface: Atomic structure of the first monolayer

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The reaction of a clean Fe{001} surface with oxygen gas was monitored with low-energy-electron diffraction (LEED) and Auger-electron spectroscopy. The formation of an Fe{001}1 × 1-O structure at full monolayer coverage was confirmed, whereas the Fe{001}$c(2 \times 2)$-O structure reported by three other groups could not be reproduced. A LEED structure analysis of the Fe{001}1 × 1-O structure revealed that the oxygen atoms are located deep inside the fourfold symmetrical hollows of the substrate surface, with the first substrate interlayer spacing 7.5% expanded with respect to the bulk. The effective hard-sphere radius of the oxygen atom in this structure is 0.78 Å. The results of the structure analysis are consistent with the results of photoemission experiments reported by others.

I. INTRODUCTION

The early stages of oxidation of the {001} face of body-centered-cubic (bcc) iron have been studied repeatedly with several surface-sensitive techniques: low-energy electron diffraction (LEED), Auger-electron spectroscopy (AES), reflection high-energy electron diffraction (RHEED), and ultraviolet photoemission spectroscopy (UPS).[1-9] There seems to be agreement between the UPS and AES investigations on the fact that in the initial stages of oxygen chemisorption the electronic structure of the Fe{001} surface is not altered, but above a threshold exposure a surface oxide is formed; there is no agreement about the exact value of the threshold.[5,7,9]

The crystallographic aspects of the phenomenon, however, are more controversial. Three groups have reported that in the chemisorption stage the oxygen produces a $c(2\times 2)$ structure, presumably at $\frac{1}{2}$ monolayer coverage,[1,5,9] and that in the surface-oxide stage the structure is 1×1, i.e., it has the same periodicities as the Fe{001} substrate. Four groups did not observe the $c(2\times 2)$ structure and reported only the observation of the 1×1 structure.[2-8] The reasons for these discrepancies in observations are not known.

The work that led to the results reported herein was undertaken with the intention of elucidating the structural (i.e., the atomic arrangement) aspects of the chemisorption process and the oxide formation. It turned out that the $c(2\times 2)$ phase could not be prepared, despite specific and repeated efforts toward that goal, whereas the 1×1 structure was always obtained easily and reproducibly. A brief account of those efforts and of the procedures followed for the preparation of the 1×1 phase is given below. A LEED structure analysis of this phase was carried out and revealed a novel aspect of surface crystallography in the form of a distortion of the substrate structure as a consequence of the absorption of oxygen. A preliminary report of the results of that structure analysis was published elsewhere.[8] We present here the details of that analysis and the refinement of the structure.

II. EXPERIMENTAL

The iron sample was the same as that used for the studies of the atomic structures of the clean Fe{001} surface[10] and of the Fe{001}$c(2\times 2)$-S structure.[11] The substrate was cleaned with a series of argon-ion bombardments and anneals as described elsewhere.[10] Exposure to high-purity (99.999%) oxygen gas was done in the LEED chamber in the dynamical mode, i.e., by leaking gas into the working chamber at rates sufficiently high to maintain the pressure at the desired level (usually 10^{-8} Torr or higher) with the pump in operation. The pump was working at maximum speed all the time, since our mass spectrometer indicated that throttling of the pump caused the appearance in the working chamber of small but noticeable amounts of CO and and that the oxygen gas was indeed most pure when the pump was not throttled at all. With the pump throttled (and hence some CO present in the chamber) we observed the appearance of diffuse $c(2\times 2)$ features at low gas exposures, which disappeared as the oxygen coverage approached one monolayer.

The *KLL* oxygen AES peak from the substrate surface was monitored during exposure to the oxygen gas. Figure 1 shows the height (defined as the distance between positive and negative ex-

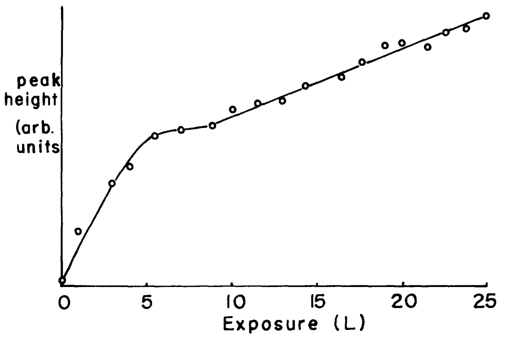

FIG. 1. Height of the doubly differentiated *KLL* oxygen AES line as a function of exposure of the Fe{001} surface to oxygen gas.

cursions) of the doubly differentiated oxygen peak as a function of exposure in langmuirs. This curve is similar to those obtained by other workers under similar circumstances.[4-5] We were particularly interested in the exposure range below 5–6 L (1 langmuir $= 10^{-6}$ Torr sec), where the Fe{001}$c(2\times 2)$-O structure has been reported to form, and we looked very carefully for anomalies in the monotonic growth of the oxygen-peak height that might reveal such formation, but we found nothing. We shall see below that the inflection point around 6 L signals the completion of the Fe{001}1×1-O structure.

Figure 2 depicts the pertinent portions of the AES spectrum obtained from the Fe{001}1×1-O phase. Immediately after conclusion of the ion bombardment and annealing process the ratio between the height of the C line at 275 eV and that of the Fe line at 652 eV was typically 0.03.[10] This ratio increased slowly with time and reached a value of about 0.05 eight hours after cleaning, which was typically the time required for collecting the full set of LEED intensity data used in this work. The AES depicted in Fig. 2 pertains in fact to a scan made *after* data collection. The appearance of an interfacial peak at 42 eV (not visible in Fig. 2) was discussed elsewhere.[12]

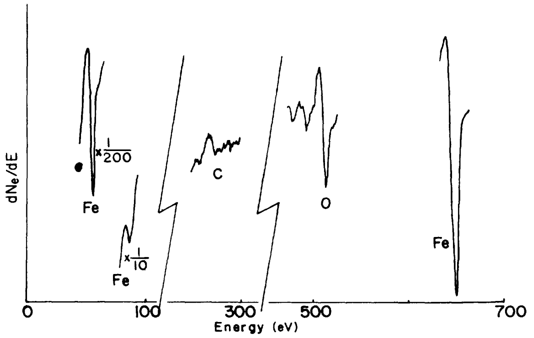

FIG. 2. Relevant portions of the AES spectrum from the Fe{001}1×1-O structure after 6 L of oxygen exposure and *after* collection of the set of LEED data tested in this work (approximately 8 h after cleaning). Primary electron energy 1.5 keV, modulating voltage 5 V peak to peak.

The LEED observations, as mentioned above, failed to reveal the oxygen $c(2\times 2)$ structure reported by others. Some faint streaking around the $\frac{1}{2}$-order positions was observed only when AES indicated the presence of larger amount of C on the surface than mentioned above. Several modifications of the oxygen-exposure procedures were tried in order to produce the $c(2\times 2)$ oxygen structure, e.g., exposure of the clean surface at room temperature, then gentle heating; exposure of the hot surface; exposure of the surface at liquid-nitrogen temperature, then slow heating to room temperature; fast exposures (higher pressures of oxygen, shorter times); and slow exposures (lower pressures and longer times). In no case was the Fe{001}$c(2\times 2)$-O structure formed by pure oxygen on a clean surface.

Exposure to oxygen caused no changes in the geometry of the LEED pattern but only changes in the intensities of the diffracted beams, which announce the formation of the Fe{001}1×1-O phase. The background remained low and the contrast high up to 6–10 L, then the background increased and the LEED spots grew progressively broader with increasing exposure. After high exposures of 25 L or more, it was always possible to revert to the Fe{001}1×1-O structure by annealing to 450–550 °C for about 1 h, but we never succeeded in reducing the oxygen concentration below one full monolayer by heating only. It may also be of interest that we obtained the same 1×1 structure using H_2O instead of O_2.

As is customary in the study of surface structures, we had to determine the precise conditions for preparation of the structure to be studied. In the present case, we monitored the 00 spectrum at $\theta = 20°$, $\varphi = 0°$ as a function of exposure and found that the intensities of several peaks, and hence the shape of the intensity vs energy curve, changed with exposure to oxygen and exhibited extrema around 6–7 L. Two examples of such changes are shown in Fig. 3, where the insert reproduces the 00 spectra for clean and oxygenated Fe{001}, respectively, while the curves through the experimental points show the changes with exposure of the intensity peaks indicated by the double arrows. These curves exhibit maxima at approximately 6 L. In accordance with previous experience with other systems[13-15] we selected 6 L as the exposure which, under the circumstances of our experiment, provided a complete and well-crystallized Fe{001}1×1-O structure.

Intensity data from this structure were collected

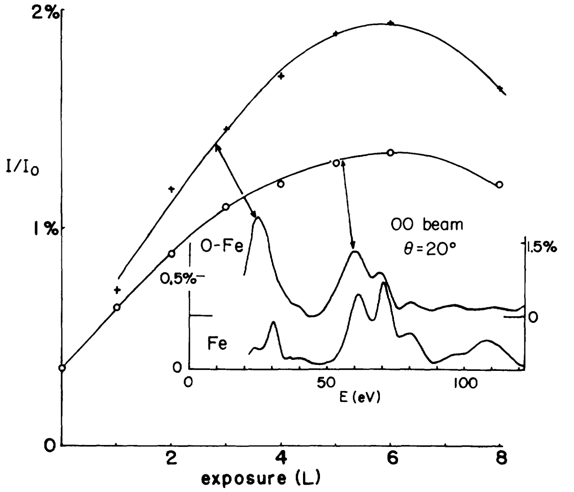

FIG. 3. Dependence upon oxygen exposure of selected peaks (double arrows) in the LEED 00 spectrum at $\theta = 20°$. The insert shows the spectra of the clear Fe{001} surface (denoted Fe) and of the Fe{001}1 × 1-O phase (denoted O-Fe), respectively.

as described elsewhere.[10] In total, 16 spectra were monitored at three different angles of incidence, i.e., at $\theta = 0°$: $\bar{1}0$, 11, 20, 21; at $\theta = 10°$, $\varphi = 0°$: 00, 10, 01, $\bar{2}0$, $\bar{1}\bar{1}$, $\bar{2}1$, 11; at $\theta = 20°$, $\phi = 0°$: 00, 01, $\bar{1}1$, $\bar{2}0$, $\bar{2}1$. Conventions for angles and beam indices have been specified elsewhere.[16] The correction for contact-potential difference was 3.7 eV, the same as for the clean Fe{001} surface.[10]

III. STRUCTURE ANALYSIS OF Fe{001}1 × 1-O

The structural model chosen postulates full monolayer coverage with a single oxygen atom lying in each of the fourfold symmetric "hollows" of the substrate surface. Within this model, the structural parameters that affect most the agreement between calculated and observed spectra are the distance d_z^S between the plane of the oxygen atoms and the plane of the first Fe layer, and the interlayer distance d_z^1 between the first and the second layer of Fe atoms.

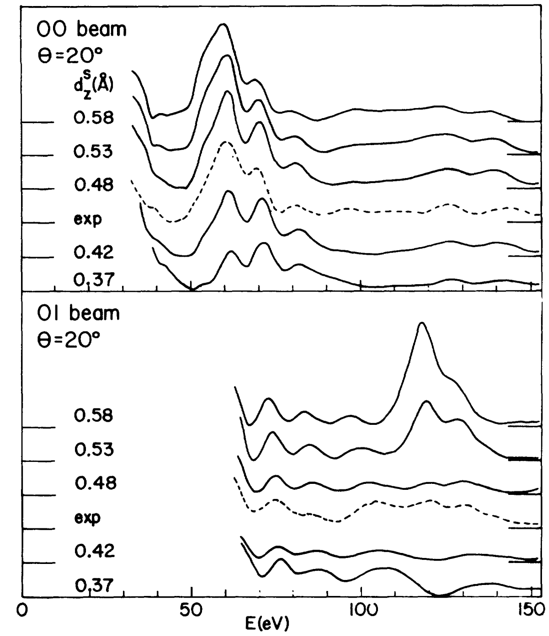

FIG. 4. Sensitivity of LEED spectra to the surface interlayer spacing d_z^S. Dotted curves are experimental.

The effect of either parameter on the calculations is exemplified in Fig. 4 for d_z^S) and in Fig. 5 (for d_z^1). The sensitivity of some spectra to d_z^S is much more pronounced here than in the cases of clean Fe{001}[10] or of Fe{001}$c(2\times2)$-S.[11] Figure 4 shows that the experimental 00 spectrum at $\theta = 20°$ (dashed curve) is matched best by $d_z^S = 0.48$ Å or larger, but the 01 spectrum at $\theta = 20°$ limits the choice to $d_z^S = 0.48$ Å The effect of the first interlayer spacing d_z^1 is equally detectable. Figure 5 shows that the experimental spectra (solid curves) are matched much better by an expansion of 7.5% in the bulk value of d_z^1 than by the bulk value itself. No amount of variation of d_z^S could improve the matching to the same extent.

We varied both d_z^S and d_z^1 independently: the former from 0.27 to 0.8 Å, the latter from +10% to −10% of the bulk value. The selection of the best pair was done both by visual evaluation of the theory-experiment fit and by the use of the $|\Delta E|$ and the intensity R factor criteria introduced elsewhere.[10] Figure 6 depicts the dependence of these two criteria and of their product upon d_z^S, showing that a minimum in the product $R|\Delta E|$

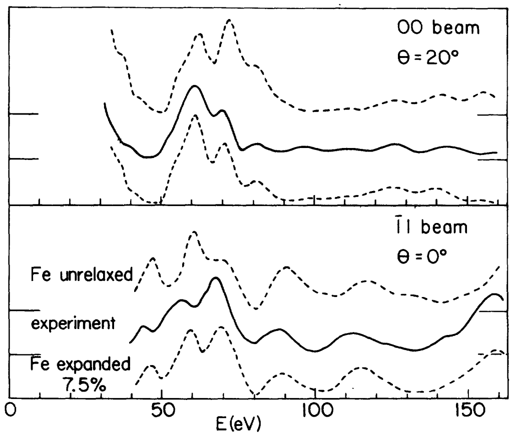

FIG. 5. Effect of first substrate interlayer spacing d_z^1 on calculated LEED spectra. Solid curves are experimental.

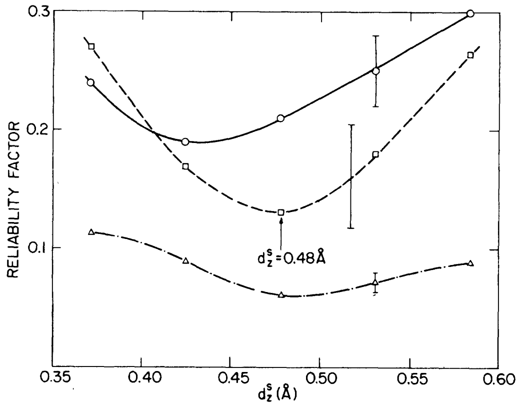

FIG. 6. Values of reliability factors: $\langle|\Delta E|\rangle$ (dot-dashed curve through triangles, ordinate scale to be multiplied by 20); R (solid curve through circles) and the product $R\ \langle|\Delta E|\rangle$ (dashed curve through squares, ordinate scale to be multiplied by 2) as functions of surface interlayer spacing d_z^S. The substrate's first interlayer spacing is 7.5% expanded with respect to the bulk.

occurs for the value $d_z^S = 0.48$ Å

The final values of both structural and nonstructural parameters used in the calculations were as follows. For the Fe{001} substrate we used a self-consistent band-structure potential for bcc iron (muffin-tin radius 1.24 Å); for the oxygen overlayer we used a superposition potential calculated from the atomic charge densities of oxygen on a bcc lattice with a muffin-tin radius of 0.83 Å. This radius was chosen as identical to the hard-sphere radius that was found for oxygen in the Fe{001}1×1-O structure as determined before refinement.[8] Experience in another system showed that the choice of a muffin-tin radius equal to the hard-sphere radius of the absorbed atom is likely to produce most reliable and physically meaningful results.[16] In the present case, the value of 0.83 Å chosen is sufficiently close to the value 0.78 Å found after refinement (see below) to justify its retention. For the imaginary parts of the potentials (bulk and surface) we used the energy-dependent values determined for the clean Fe{001} surface.[10] The inner potential was chosen to be 12 eV, equal in the bulk and on the surface.

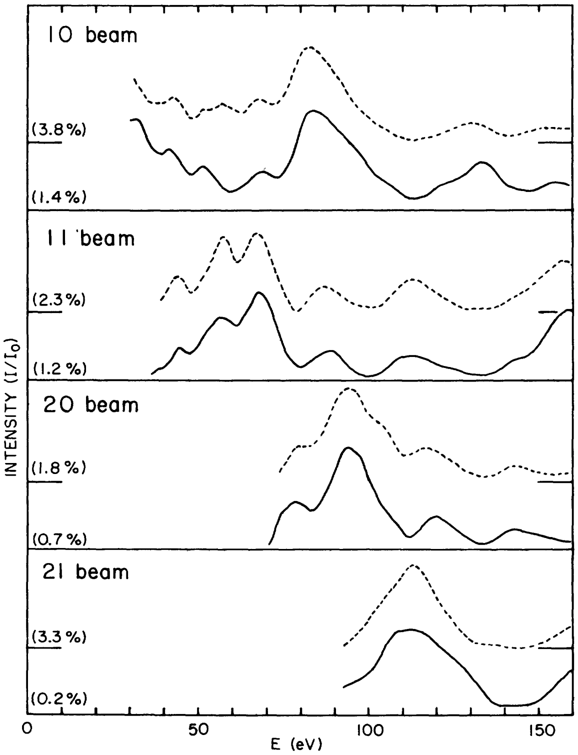

FIG. 7. Final comparison between calculated and observed LEED spectra: $\theta = 0°$. The numbers in percent give the intensity of the highest peak in the corresponding spectrum.

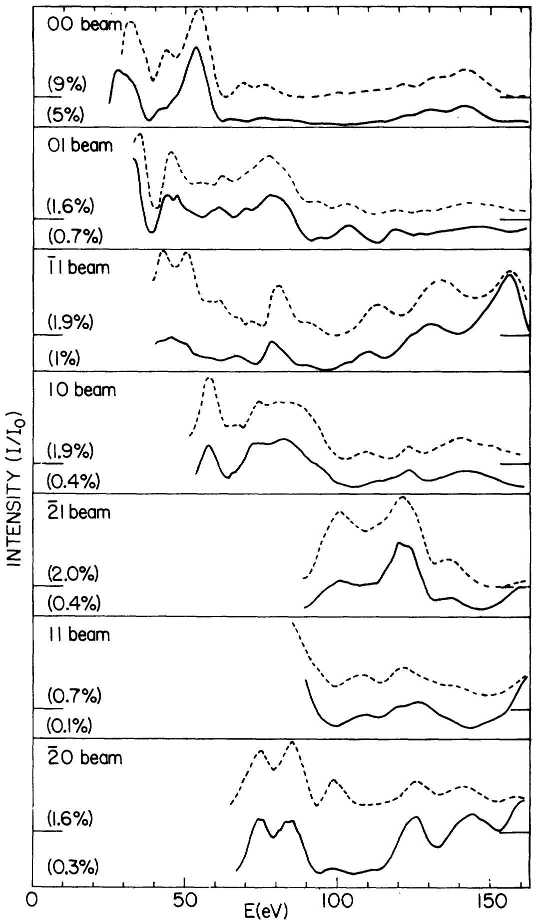

FIG. 8. Final comparison between calculated and observed LEED spectra: $\theta = 10°$, $\phi = 0°$. The numbers in percent give the intensity of the highest peak in the corresponding spectrum.

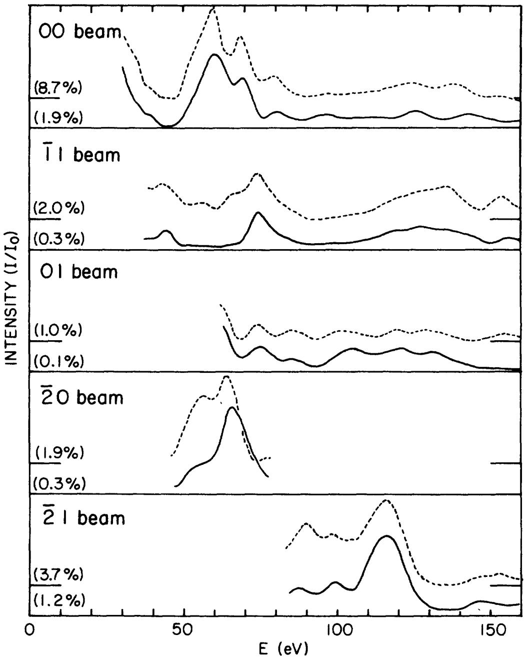

FIG. 9. Final comparison between calculated and observed LEED spectra: $\theta = 20°$, $\phi = 0°$. The numbers in percent give the intensity of the highest peak in the corresponding spectrum.

The mean vibrational amplitude $(\langle u^2 \rangle)^{1/2} = 0.115$ Å was again chosen equal to the value used in the clean-surface study.[10] The surface interlayer spacing d_z^s was 0.48 Å and the first substrate interlayer spacing d_z^1 was 1.54 Å, or 7.5% expanded with respect to the bulk value 1.43 Å.

The LEED spectra calculated with the above paramenters compare very satisfactorily with their experimental counterparts, as can be seen in the Figs. 7–9 for $\theta = 0°$, $10°$, and $20°$, respectively.

IV. DISCUSSION

A hard-sphere model of the final structure is presented in Fig. 10 in terms of a cross section along (110) on the Fe(001) substrate. We see that the effective radius of the oxygen atom is 0.78 Å, somewhat larger than Pauling's covalent radius of 0.66 Å but very close to the value 0.73 Å found in the Ni{001}$c(2\times2)$-O structure.[17]

The expansion of the first substrate interlayer spacing is the first confirmed case of a distortion of a substrate lattice caused by chemisorption of foreign atoms.[18] LEED analysis of data from clean Fe{001} suggests the the first interlayer spacing is contracted by 1.4% with respect to the bulk spacing with an uncertainty of ±3% of the interlayer spacing.[10] Hence, the 7.5% expansion found in the present work for Fe{001}1×1-O represents an overall increase of 9% with respect to the first interlayer spacing of clean Fe{001}. In terms of the hard-sphere model, the distortion may be explained by the fact that the small oxygen atom "sinks" into the fourfold symmetric hollow on the substrate surface until it comes to rest on top of the iron atom in the second layer. There seems to be a tendency toward formation of a planar Fe-O layer as in the bulk of the rocksalt-type FeO crystal. Since the oxygen atom cannot penetrate deeper into the bulk without radically disrupting the substrate structure, the planar bonding arrangement in FeO can only be approached by lifting the first iron layer away from the second. This crystallographic distortion is very probably correlated with the changes in the electronic structure of Fe{001} that have been observed by photoemission and have been interpreted as heralding the "nucleation of a surface oxide."[5,7,9]

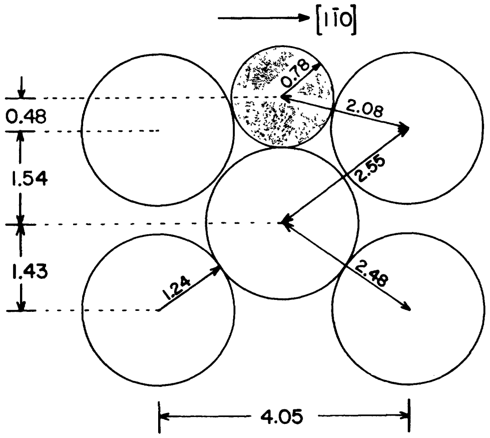

FIG. 10. Hard-sphere model of the neighborhood of an oxygen atom in the Fe{001}1×1-O structure. Cross section along (110) plane. Distances in angstroms. Note the expansion of the first substrate interlayer spacing (1.54 Å) with respect to the bulk (1.43 Å).

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