Bonding of Oxygen on Al(111): A Surface Extended X-Ray Absorption Fine-Structure Study

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(Received 13 September 1979)

The initial ordered chemisorption stage of oxygen on Al(111) has been investigated using polarization-dependent surface extended x-ray absorption fine-structure measurements above the O K absorption edge. The O-Al bond length in the threefold hollow adsorption site has been determined to be 1.79 ± 0.05 Å. A strong polarization dependence of the extended x-ray absorption fine-structure signal allows the determination of the O-O distance (2.90 ± 0.05 Å) between the chemisorbed oxygen atoms.

The existence of an ordered (1×1) configuration of oxygen on Al(111) at small exposures [≲1000 L (1 L = 1 μTorr sec)] has been well established by photoemission[1,2] and low-energy electron-diffraction (LEED)[1,3,4] studies. Experimental[1-4] and theoretical[5] studies reveal that oxygen chemisorbs in the threefold hollow site outside[6,7] the Al(111) surface. One of the important parameters which has so far escaped an accurate determination is the O-Al bond length R (or equivalently the oxygen distance Z above the surface). In all theoretical calculations Z is treated as an adjustable parameter; and, depending on the nature of the calculation or the minimization criterion used, widely different Z values have been reported. Lang and Williams[8] obtained $Z = 1.75$ Å by minimizing the total system energy of a simple atom-jellium model and $Z = 1.32$ Å when Al pseudopotentials were included to first order.[9] Salahub, Roche, and Messmer[5] carried out a self-consistent-field $X\alpha$ scattered-wave molecular-orbital calculation for oxygen on an Al(111) cluster and compared the calculated valence bands to the photoemission spectra of Flodström *et al.*[1] Within the accuracy limits of theory and experiment, agreement was found at a Z value between 0.53 Å and 1.06 Å. Recently, a dynamical (multiple scattering) LEED analysis of spectra of oxygen on Al(111) recorded at monolayer coverage (~150 L) has been reported yielding $Z = 1.33$ Å.[4]

The inconsistency of the above results has led us to investigate the system oxygen on Al(111) at monolayer coverage with a technique which is capable of accurately determining atomic separations in solids and on surfaces. The extended x-ray absorption fine-structure (EXAFS)[10] measurements reported here which were carried out in the surface-sensitive electron-yield detection mode[11,12] reveal an O-Al chemisorption bond length of $R = 1.79 \pm 0.05$ Å which corresponds to a Z value of $0.70^{+0.10}_{-0.15}$ Å. These numbers can now serve as a standard for future calculations. We also report for the first time polarization-dependent effects[13] in *electron-yield* EXAFS measurements which allow us to determine the O-O separation in the ordered overlayer on Al(111). The O-O distance found is 2.90 ± 0.05 Å in agreement with a (1×1) oxygen overlayer configuration.

Experiments were performed at the Stanford Synchrotron Radiation Laboratory using the Grasshopper monochromator.[14] The Al(111) single crystals were cleaned *in situ* (base pressure 1×10^{-10} Torr) by repeated Ar^+ bombardment and annealing cycles. The clean and oxygen-exposed surfaces were characterized by LEED and core-level photoemission spectra. The latter agreed with those reported in the literature.[1] Surface EXAFS spectra were recorded by detecting the total electron yield from the sample.[15] The electron detector consisted of two hemispherical grids and a Spiraltron electron multiplier. Experimental details will be reported elsewhere.[16]

The surface EXAFS signal $\chi(k)k^2$ above the O K absorption edge for a sample of 100 L oxygen on Al(111) is shown in Fig. 1 for two polarization directions. Here θ is the x-ray angle of incidence from the Al(111) surface which for our experimental geometry (p polarization) is also the angle between the electric field vector $\vec{E}$ and the sample normal. The signals shown were obtained from the raw data by the data reduction procedures discussed in Ref. 15. The oscillations in Fig. 1(a) ($\theta = 11°$) are very nearly sinusoidal while those in Fig. 1(b) ($\theta = 45°$) exhibit a strong nonperiodic beat. Such behavior is characteristic for systems where more than one neighbor shell contributes to the EXAFS signal. The strong polarization dependence is most clearly evident at a wave vector of $k \sim 7.5$ Å^{-1} where the two signals in Fig. 1 are completely out of phase.

The Fourier transforms of the noisy EXAFS signals $\chi(k)k^2$ in Fig. 1 are shown as solid lines in Fig. 2. Also shown as a dashed line in Fig. 2(b)

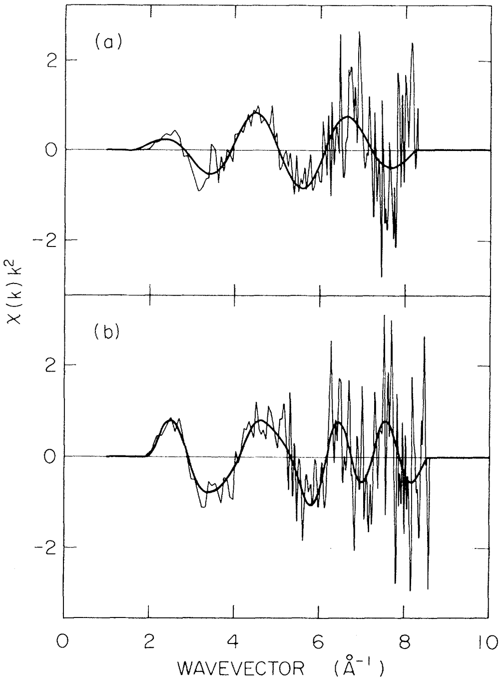

FIG. 1. (a) EXAFS signal $\chi(k)k^2$ above the oxygen K edge for a sample of 100 L O_2 on Al(111) and $\theta = 11°$ where θ is defined in Fig. 3. The noisy signal is the original data. The smooth line represents the main frequency and is the Fourier-filtered signal corresponding to peak A in Fig. 2(a). (b) Same as in (a) for $\theta = 45°$. The smooth line represents the two superimposed dominant frequencies corresponding to the Fourier-filtered nearest-neighbor peaks A and B in Fig. 2(b).

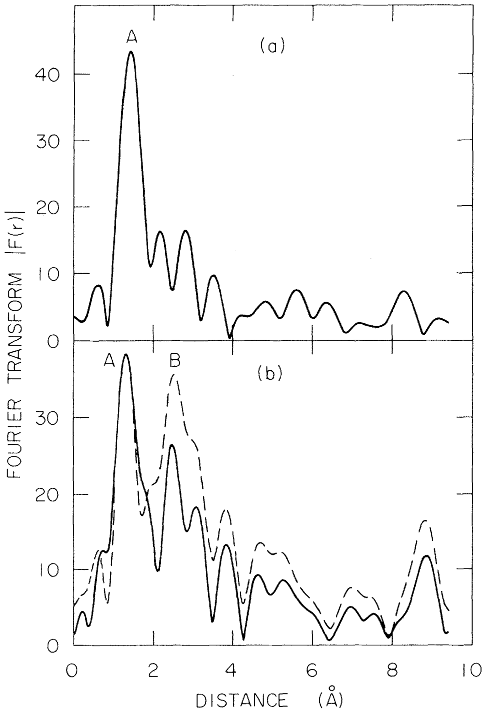

FIG. 2. (a) Absolute value of the Fourier transform $|F(r)|$ of the noisy EXAFS signal in Fig. 1(a). Note that the peaks in $|F(r)|$ are displaced from the true distance by a phase shift. (b) $|F(r)|$ of the noisy signal $\chi(k)k^2$ in Fig. 1(b) (solid line) and of the signal $\chi(k)k^3$ (dashed line).

is the transform of the EXAFS oscillations $\chi(k)k^3$ which enhances the contribution from the high-k region of the signal. The transform for $\theta = 11°$ in Fig. 2(a) is dominated by a single peak, A. This peak is also observed for $\theta = 45°$. In addition, for this polarization a second strong peak, B, is observed which for the $\chi(k)k^3$ weighted signal has almost the same intensity as peak A. At a slightly higher oxygen exposure of 150 L, peak B becomes weaker with respect to peak A. We have filtered out peak A in Fig. 2(a) and peaks A plus B in Fig. 2(b) and transformed them back into k space. The so obtained filtered EXAFS signals are shown as smooth solid lines in Fig. 1.

Peak A is attributed to the nearest-neighbor O-Al distance (see Fig. 3). This distance can be determined provided the photoelectron scattering phase shift is known for the O-Al system. In our analysis we used a phase shift derived from a sample of amorphous aluminum oxide for which the O-Al distance was known from x-ray diffraction. The results of this analysis are summarized in Table I. We also analyzed our data with theoretically calculated phase shifts[17] which yielded slightly shorter (~ 0.05 Å) O-Al distances than those reported in Table I. This is consistent with previous findings for the O-Si system[15] where calculated phase shifts underestimated the true distance by ~ 0.03 Å. The obtained distances in the range of monolayer coverage (100–150 L oxygen) all lie within 0.05 Å. However, the value for 100-L O_2 exposure and $\theta = 45°$ is shorter than the other three. For this case the EXAFS signal [Fig. 1(b)] is more complex and the interference of the signals from the first- and second-neighbor shell [peaks A and B in Fig. 2(b)] might cause a slight error in the distance determination, especially with the limited k range available. Another factor which has been ignored so far is the presence of smaller amounts of an oxidelike phase in addition to the chemisorbed oxygen on Al(111). This phase would contribute least to the EXAFS signal for the 100-L O_2 expo-

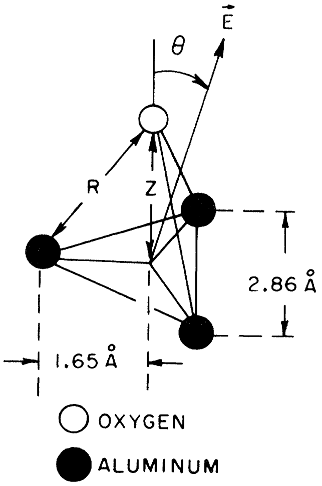

FIG. 3. Model of oxygen chemisorbed in the threefold hollow site on the Al(111) surface. R is the O-Al nearest-neighbor distance, Z the distance above the Al surface plane, and θ the angle between the macroscopic electric-field vector and the surface normal.

TABLE I. Derived bondlengths for oxygen on Al(111).

Oxygen exposure (L)	θ^a	O-Al Distance (Å)	O-O Distance (Å)
100	11°	1.81	
100	45°	1.76	2.90
150	11°	1.80	
150	45°	1.81	2.95

[a] See Fig. 3.

sure, $\theta = 45°$ case in Table I.[16] Thus, the slightly shorter distance for this case might be the more accurate value for the O-Al chemisorption bond length. We allow for this possibility by conservatively quoting a value of 1.79 ± 0.05 Å for the O-Al distance. As shown in Fig. 3 this value corresponds to a vertical separation of $Z = 0.70^{+0.10}_{-0.15}$ Å from the outermost plane of Al nuclei, assuming chemisorption in the threefold hollow site.

Peak B is assigned to the O-O distance in the chemisorbed overlayer. Since the oxygen atoms lie in a plane parallel to the surface, O-O scattering does not contribute to the EXAFS signal for an $\vec{E}$ vector orientation perpendicular to the surface ($\theta = 0°$).[13] For our geometry the intensity I of the signal due to O-O scattering should follow an $I \sim \cos^2(90° - \theta)$ relationship. It should thus be negligible at $\theta = 11°$ ($I = 3.6 \times 10^{-2}$) but significant at $\theta = 45°$ ($I = 0.5$), in agreement with the fact that peak B is only observed at $\theta = 45°$. While it is clear from the polarization dependence that peak B corresponds to a distance between atoms which lie parallel or nearly parallel to the surface plane we still need to examine whether it could be due to O-Al second-nearest-neighbor scattering. For O atoms in the threefold hollow site and a distance of 0.7 Å outside the surface plane, the three second-nearest-neighbor Al atoms are 3.37 Å away. Peak B falls at a distance around 2.9 Å with either O-O or O-Al scattering phase shifts. We can thus exclude this possibility. We note, however, that the shoulder on the right-hand side of peak B in Fig. 2(b) (dashed curve) corresponds to a distance of ~3.4 Å and might thus indicate the three Al second-nearest neighbors. Using a calculated O-O phase shift[17] we find peak B to correspond to a distance of 2.90 ± 0.05 Å. This value is in excellent agreement with the expected 2.86-Å separation from a given chemisorbed O atom to its six nearest O neighbors in a (1×1) overlayer. We note that the derived distance is also distinctively different from the 2.72 Å second-nearest O-O distance in aluminum oxide.[12]

The present result for the bonding distance of O on Al(111) $R = 1.79 \pm 0.05$ Å strongly disagrees with the previously reported LEED value[4] of $R = 2.12 \pm 0.05$ Å. We note that the latter R value would be truly exceptional as judged from available O-Al bond lengths in bulk crystals or molecules.[18] Our results also indicate deficiencies in atom-jellium-type calculations even when pseudopotentials are included to first order since such calculations predict $R \geq 2.12$ Å.[8,9] On the other hand, our results are in excellent agreement with the prediction made from self-consistent-field $X\alpha$ scattered-wave molecular-orbital calculations[5] which compared the calculated electronic valence-band structure to that obtained experimentally from photoemission measurements.[1] This lends strong credibility to the potential of such calculations to calculate the electronic structure of surface complexes from first principles provided the structural parameters are known. Our derived value for the O-O separation in the chemisorbed overlayer is in good agreement with previous LEED[1,3,4] and photoemission[2] results of a (1×1) oxygen arrangement. It appears that a consistent picture of the structural and electronic properties of the (1×1) oxygen surface on Al(111) does now exist.

We have greatly benefitted from the experimen-

tal help of S. Brennan, M. Hecht, and J. N. Miller. We would like to thank I. Lindau and W. E. Spicer for providing the data acquisition system.

This work was partly supported by the National Science Foundation under Contract No. DMR 77-27489 in cooperation with SLAC and the Basic Energy Division of the Department of Energy.

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Evidence for Possible Electronic Contributions to the W(001) Surface Phase Transition

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(Received 10 September 1979)

The calculated surface generalized susceptibility, determined from *ab initio* self-consistent thin-film energy bands for the unreconstructed phase of W(001), displays a prominent peak at $\bar{M}$ when matrix elements and local-field corrections are included and supports proposed charge-density-wave interpretations of the observed reconstruction to the $c(2\times2)$ phase. These results are consistent with the Debe and King parallel-shift model and the suggestion that W(001)$c(2\times2)$-H at room temperature represents an impurity-stabilized substrate reconstruction.

Surface-structural phase transitions are becoming a subject of intense experimental and theoretical investigation. A prototypical example is given in the low-energy-electron-diffraction (LEED) studies of the tungsten[1,2] (001) surface which show a temperature-dependent phase transition to a $(\sqrt{2}\times\sqrt{2})R45°$ or $c(2\times2)$ structure when the temperature is lowered below about 300 K. This transformation seems to be of second order and is reversible on varying only the temperature. [A similar transition has been observed on Mo(001).[2]] Recent investigations[1,2] conclude that chemisorbed impurities (hydrogen in particular) need not be present on the surface when the $c(2\times2)$ structure is observed, thus implying that the transition is characteristic of the clean surface.

Felter, Barker, and Estrup[1] and Debe and King[2] have suggested that relatively small periodic distortions could account for the phase transition, and they have noted that this is compatible with a charge-density-wave (CDW) mechanism as in the layered transition-metal dichalcogenides. A LEED intensity analysis[3] for W(001) at 100–140 K supports a model proposed by Debe and King[4] in-