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Surface x-ray-diffraction study of the Rh(111)+(2×2)-3CO structure

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We have studied the geometry of the high-coverage Rh(111)+(2×2)-3CO structure by surface x-ray diffraction. Analysis of the in-plane data set reveals three evenly separated CO molecules per (2×2) unit cell. The evaluation of the crystal truncation rods shows that one CO molecule resides in an on-top site while the other two CO molecules occupy hollow sites. The intensity modulations of the out-of-plane fractional order rods provide geometrical information about distances between the C and O atoms and on the buckling of the CO overlayer. [S0163-1829(99)10107-3]

I. INTRODUCTION

The study of CO adsorption on single-crystal transition-metal surfaces has received much attention for a long time.[1] This is partly due to the need to understand the elementary steps in heterogeneous catalytic reactions (Rh for instance catalyzes efficiently the oxidation of CO), but it is also related to comprehend the interaction of these simple molecular adsorbates with each other and the transition-metal surface. In order to understand these interactions a knowledge of the geometrical structure of these adsorption systems is mandatory.

The adsorption of CO on the Rh(111) surface results in several well-ordered overlayer structures depending on CO coverage and sample temperature.[2–8] At temperatures below 120 K the following overlayer structures are observed when the Rh(111) surface is exposed to CO: (2×2)-CO, $(\sqrt{3}\times\sqrt{3})R30°$-CO, (4×4)-8CO, and at saturation a (2×2)-3CO, corresponding to coverages of 0.25, 0.33, 0.5, and 0.75 ML (one ML equals the number of atoms in the surface plane) of CO, respectively. This complex adsorption system has been studied by a number of different techniques such as thermal desorption spectoscopy,[2,6] low-energy electron diffraction[3,5,9] (LEED), electron-energy loss spectroscopy[4] (EELS), helium diffraction[7] (HeD), and high resolution core level spectroscopy[8] (HRCLS). For CO coverages up to 0.33 ML, the different investigations have agreed that the CO molecules adsorb in on-top sites on the Rh(111) surface. For the (2×2)-3CO, previous EELS (Ref. 4) and LEED (Ref. 5) studies lead to a structural model with two CO molecules in (nearly) on-top sites and one CO molecule in bridge position (hereafter denoted bridge model). This structural model was recently challenged by HRCLS (Ref. 8) and HeD studies.[7] Instead, these investigations indicated that one CO molecule occupies an on-top site while the two remaining molecules in the unit cell occupy threefold hollow sites (hereafter denoted hollow model). Indeed, the original LEED data from the (2×2)-3CO was recently reanalyzed[9] and the conclusions drawn from HRCLS and HeD could be confirmed.

With the introduction of third generation synchrotrons for x-ray production, the technique of surface x-ray diffraction (SXRD) became a powerful tool to investigate not only the surface geometry resulting from adsorption of heavy elements, but also surface structures resulting from adsorption of lighter elements, such as CO.[10,11] SXRD should be able to determine the detailed geometry of surface structures, which may be difficult to investigate with more traditional surface-structure techniques such as LEED. The CO/Rh is such a system since the CO overlayer degrades rapidly on the Rh(111) surface when exposed to an electron beam. Furthermore, the weak interaction between the x rays and the sample allows simple single-scattering theory to be applied for the evaluation of the data,[12] which ensures fast calculations during the data analysis.

In the present investigation we have studied the (2×2)-3CO structure by using SXRD. The results confirm that the (2×2) unit cell contains one CO molecule occupying an on-top position and two CO molecules in threefold hollow sites. A more profound buckling of the CO overlayer is found than in the previous LEED study.[9] The topmost Rh layer is found to relax outwards.

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II. EXPERIMENT

The experiments were performed during two different runs at the surface diffraction beamline at the European Synchrotron Radiation Facility. This beamline has been described elsewhere.[13] During the analysis of the first data set it turned out that the (2×2)-3CO structure could not be determined unequivocally. Therefore, in a second run additional data were collected. The incoming x-ray beam was generated by an undulator and monochromatized by a double crystal Si(111) monochromator cryogenically cooled and sagittally focusing. The energy was set to 14 and 12 keV for the two different runs, respectively. The Rh sample was mounted in an UHV system coupled to a six-circle diffractometer operated in the z-axis mode. The base pressure in the experimental chamber was about 2×10^{-10} Torr. The Rh(111) surface was cleaned by Ar^+ sputtering at a sample temperature of approximately 900 K followed by annealing at 1500 K in order to restore the surface order. Residual carbon was removed by keeping the crystal at temperatures between 400 and 1000 K in an oxygen atmosphere of about 10^{-9} Torr. The crystal temperature was measured by a Ni-Cr-Ni thermocouple spotwelded to the side of the crystal. It is to note that the same Rh(111) sample and the same cleaning procedure were used in the present investigations as in the recent HRCLS studies.[8] Cooling to approximately 120 K was achieved with a liquid nitrogen open-loop cryostat. The (2×2)-3CO structure was formed by keeping the Rh crystal at 250–300 K in a CO atmosphere of around 1×10^{-6} Torr up to saturation and subsequent cooling to around 120 K. A background pressure of CO of around 1×10^{-8} was maintained during measurements in order to ensure the stability of the structure. Under these conditions, no time-dependent changes in the diffracted fractional order intensities were observed for several hours.

The diffracted intensities I_{HKL} were collected by a scintillator detector by orienting the sample and detector to fulfil an (H,K,L) diffraction condition and then rotating the sample at positive and negative angles q around its surface normal. The integrated measurements $I_{HKL}=|F_{HKL}|^2$ was obtained by integration over the q scans after the scans had been corrected for Lorentz factor, polarization, and active sample area. A total of 233 reflections F_{HKL} were collected resulting in a total of 175 symmetry in-equivalent structure factor data. The average agreement factor derived from the strongest reflections, i.e., from 25 (59 measurements) reflections using the $P3M1$ symmetry, was found to be 4.7%. Possible sources for a nonvanishing agreement factor are sample misalignment, sample quality, diffractometer imperfections, etc. The $P3M1$ symmetry is the maximum symmetry of the clean Rh(111) surface. The agreement factor obtained when using the $P6MM$ symmetry was 8.7%, indicating that the actual plane group of the Rh(111)+(2×2)-3CO surface is indeed $P3M1$.

III. RESULTS AND DISCUSSION

The in-plane diffraction data were collected with an angle of incidence of 1° and small exit angle in order to ensure a perpendicular momentum transfer L close to zero ($L=0.2$ corresponding to an exit angle of 1.34°). A total of 37 structure factor data were collected in plane, as presented in Fig. 1, resulting in 19 symmetry in-equivalent reflections with an agreement factor of 6.4% (using the $P6MM$ symmetry in this case gave an agreement factor of 8%). Figure 1 shows graphically the intensities of the measured in-plane reflections. The radii of the empty (data) semicircles in Fig 1 are proportional to F_{HK} and the areas to the integrated intensities. The (1/2,1/2,0.2) reflection had a peak counting rate of approximately 4500 counts/s. The (1/2,0,0.2)- and the (0,1/2,0.2)-order reflections was found to be approximately 15 times weaker than the (1/2,1/2,0.2)- and the (1,−1/2,0.2)-order reflections. It should be noted that the (1/2,0)- and the (0,1/2)-order reflections would not have been observed if L would have been exactly zero, since these reflections are due to the buckling between the different CO molecules in the direction perpendicular to the surface. The filled semicircles in Fig. 1 correspond to the optimized calculated values from the favored model as described below. The values of χ^2 between experimental and the calculated structure factors[12] for the in-plane data only were found to be 0.79 for the hollow model as compared with 0.95 for the bridge model. From the mere intensity modulation of the in-plane data it is clear that the CO molecules are evenly dispersed in the (2×2) unit cell. Since Rh is a much stronger scatterer than C and O, lateral relaxations of substrate atoms can clearly be ruled out.

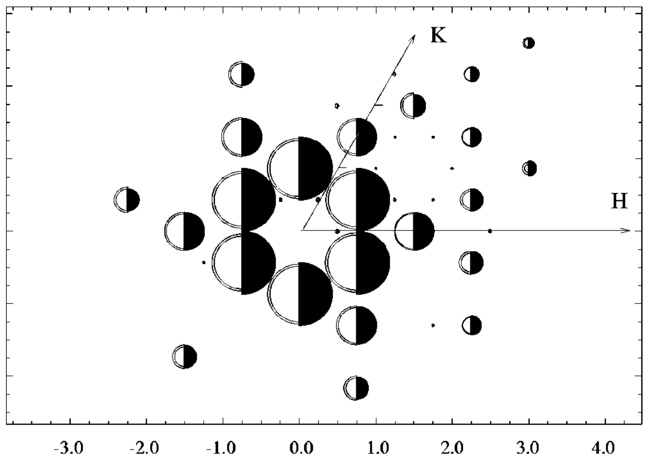

FIG. 1. In-plane structure factors, the radius of the empty semicircles are proportional to the measured in-plane structure factors. The uncertainties are indicated by the two radii. The filled semicircles corresponds to the structure factor calculated from the optimum geometry (the hollow model) as discussed in the text.

From the measured in-plane structure factors, the surface pair-correlation function, i.e., the Patterson function, may be calculated from

$$P(x,y)=\sum_{HK}|F_{HK}|^2\cos 2\pi(Hx+Ky).$$

The result is illustrated as a two-dimensional contour plot in Fig. 2 together with the vectors corresponding to a 2×2 unit cell of the (2×2)-3CO. Figure 2 implies directly that there are three evenly dispersed CO molecules per 2×2 unit cell.

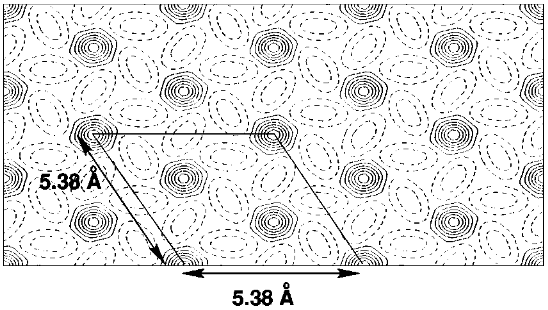

FIG. 2. Experimentally determined Patterson map from the in-plane structure factor data.

However, no additional information concerning the favored adsorption sites of the CO molecules is provided.

Additional information on the adsorption geometry of the CO molecules is gained by evaluating the structure factors of out-of-plane reflections from the crystal truncation rods (CTR's).[10] Such reflections are known to be sensitive to the registry of the CO overlayer with respect to the substrate.[10] In Fig. 3(a) examples of such integral-order rods are compiled, the $(1,1,L)$, the $(2,2,L)$, and the $(2,1,L)$ rods. In the figure are also shown the optimized fits for the hollow model (full line) and the bridge model (dot-dashed line). It may directly be seen that the hollow model yields a bettor fit to the experimental data and this model is therefore the preferred. The χ^2 obtained for the hollow model was found to be 1.25 as compared to 1.95 for the bridge model. The $(1,1,L)$ rod and the $(2,2,L)$ rod corresponds to directions in reciprocal space that contains essentially the same information. In these directions, a strong contribution due to the CO overlayer should be present. The major difference between the two models is manifested in the $(1,1,L)$ rod as a larger value of the structure factor in the minimum of the CTR and a smaller value at high L values for the bridge model. Similar but less-pronounced differences are observed in the case of the $(2,2,L)$ rod.

Having established the adsorption sites of the CO molecules, we turn to the detailed adsorption geometry. In Fig. 3(b) are shown examples of the fractional-order rods measured, namely the $(1/2,1/2,L)$, $(3/2,0,L)$, and the $(5/2,1,L)$ rods. These rods contain information from the CO overlayer and the CO-induced relaxations of the substrate layers. Again, the optimized fits for the hollow model (full line) and the bridge model (dot-dashed line) are included in the figure. The χ^2 obtained in this case for the hollow model is 1.5 as compared with 1.8 for the bridge model. This again is in favor of the hollow model. The distance between maxima and minima in these rods is directly related to the perpendicular distances between the C and O atoms. Since the internal CO bond length is identical in both models, the only difference between the bridge and the hollow model could occur if the buckling of the CO molecules is different for the two models. In addition, since the structure factors from these rods are only due to the CO molecules, these structure factors are insensitive to the registry of the CO overlayer with respect to the substrate. Therefore, is it interesting to compare the particular values for the buckling within the CO overlayer. The best fit geometries of the two models reveal no major difference in the buckling of the CO overlayer for the two models. The layer spacing difference between the CO molecules adsorbed in on-top and threefold hollow sites for the hollow model was found to be 0.38 Å, while the layer spacing difference between the CO in on-top (nearly) sites and in bridge sites in the bridge model was found to be 0.37 Å.

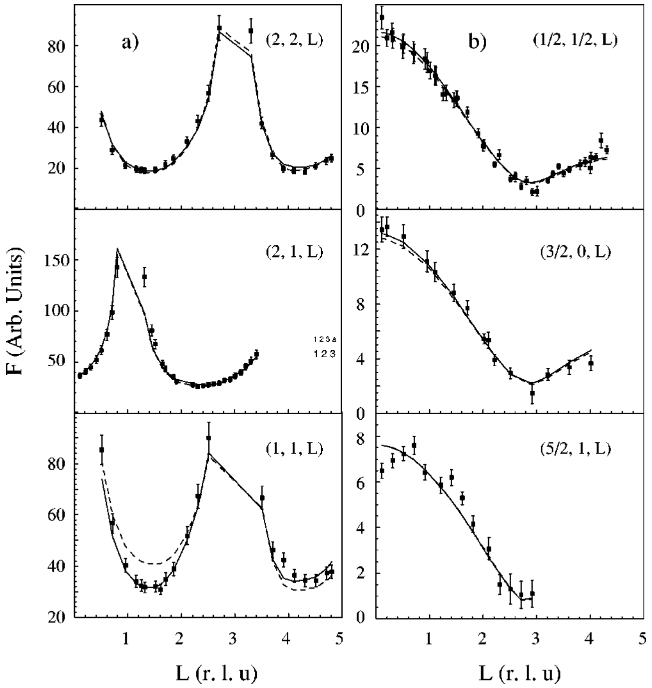

FIG. 3. (a) Measured structure factors versus perpendicular momentum transfer L for the $(1,1,L)$, $(2,1,L)$, and the $(2,2,L)$ integer order rods. (b) Measured structure factors versus perpendicular momentum transfer L for the $(1/2,1/2,L)$, $(3/2,1,L)$, and the $(5/2,1,L)$ fractional order rods. The continuous lines are calculated by using the hollow model, the dashed using the bridge model.

The optimum geometry for CO adsorbed in the hollow model is shown in Fig. 4 and detailed in Table I. The final χ^2 with all data included was found to be 1.3 for the hollow model and 1.8 for the bridge model.

From the above results it is clear that the adsorption sites found in this study agree with the sites found previously with LEED.[9] It should be emphasized that the overall agreement of the structural parameters obtained by LEED and SXRD is good (cf. Table I). The major disagreement, although small, is found for the distance between the on-top CO molecule and the Rh atom directly underneath. The first Rh layer spacing of 2.26±0.03 Å is expanded by 3% with respect to the bulk value of 2.19 Å, which is in excellent agreement with the LEED study. However, it should be noted that any kind of superstructure reconstruction in the Rh layers would dominate the structure factors of the fractional-order rods. Therefore, from the present investigation a small buckling in the Rh layers can safely be excluded, we do not observe the reported buckling[9] in the second Rh layer. Similarly, using different Debye-Waller factors for the Rh atoms in the topmost substrate layer can be ruled out.

We will now turn to a brief discussion of the utility of SXRD for the structure determinations of surfaces covered by low atomic number elements, such as CO. The (2×2)-3CO overlayer is a particular suited system, since the

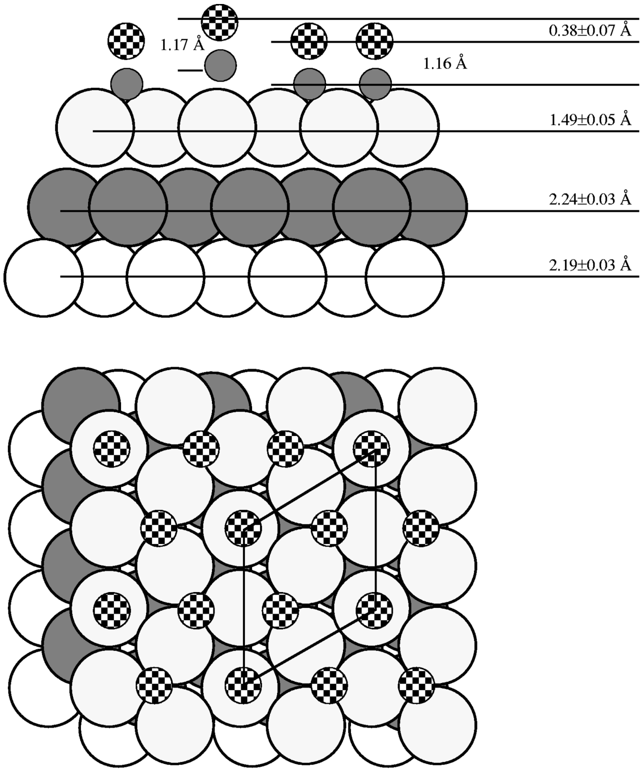

FIG. 4. Optimum geometry found for the Rh(111)+(2×2)-3CO structure, with CO on top and threefold hollow fcc and hcp sites. The upper diagram shows a side view while the bottom shows a plan view.

TABLE I. Atomic coordinates perpendicular to the surface for the optimum fit geometry of Rh(111)+(2×2)-CO. The results from a low-energy electron diffraction study (Ref. 9) are included for comparison.

Atom	SXRD	LEED
1 O (CO on top)	0	0
2 C (CO on top)	−1.17±0.07	−1.15±0.07
3 O (CO hcp)	−0.38±0.07	−0.33±0.07
4 C (CO hcp)	−1.54±0.07	−1.51±0.07
5 O (CO fcc)	−0.38±0.07	−0.33±0.07
6 C (CO fcc)	−1.54±0.07	−1.49±0.07
7 Rh	−2.91±0.03	−2.98±0.04
8 Rh	−2.91±0.03	−2.98±0.04
8 Rh	−2.91±0.03	−2.98±0.04
8 Rh	−2.91±0.03	−2.98±0.04
9 Rh	−5.15±0.03	−5.24±0.04
9 Rh	−5.15±0.03	−5.24±0.04
9 Rh	−5.15±0.03	−5.24±0.04
9 Rh	−5.15±0.03	−5.24±0.04
10 Rh	−7.33±0.03	−7.43±0.06
10 Rh	−7.33±0.03	−7.43±0.06
10 Rh	−7.33±0.03	−7.43±0.06
10 Rh	−7.33±0.03	−7.43±0.06

underlying Rh(111) substrate is not reconstructed nor relaxed. Therefore, the CO structure could be determined. However, simulations showed that even different Debye-Waller factors in the topmost Rh layer would significantly interfere with the analysis. These simulations showed that the different scattering factors (due to temperature effects) of the Rh atoms give rise to x-ray intensities, which are as high as those from the bare CO overlayer. Therefore, one has to be very careful in determining the structure of low atomic number elements, in particular its temperature behavior. The introduction of anisotropic temperature effects of CO in the analysis may improve the fit,[10] however the significance of the resulting mean-square displacements is at least doubtful. Altogether the structure determination of low atomic number elements on metal surfaces is quite demanding in terms of the size and quality of the experimental x-ray diffraction data. Therefore, obtaining precise and detailed information on perpendicular distances in adsorbed small molecules is probably not the domain of SXRD even if using third-generation synchrotron facilities. However, the determination of bigger molecules, whose adsorption geometry is dominated by lateral parameters, such as a flat-laying molecule (benzene) may be well suitable for SXRD.

In summary, we have determined the adsorption geometry of the Rh(111)+(2×2)-CO surface structure. The in-plane data set reveals three CO molecules per (2×2) unit cell whereas crystal truncation rods show that one CO molecule per (2×2) unit cell resides in an on-top site while the remaining two CO molecules occupies hollow sites. The out-of-plane fractional-order rods are shown to give information on the distances between the C and O atoms and on the buckling of the CO overlayer. No superstructure of the topmost Rh layer is observed. The applicability of SXRD to determine surface structures induced by low atomic number elements was briefly discussed.

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