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Catalysis Studies

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CATALYSIS STUDIES

by

T. N. Taylor and W. P. Ellis

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ABSTRACT

The New Research Initiatives Program (NRIP) project on catalysis in Los Alamos Scientific Laboratory (LASL) Group CMB-8 has made significant progress towards performing the first basic in situ experimental studies of heterogeneous catalysis on solid compound surfaces in a LEED-Auger system. To further understand the surface crystallography of a possible catalyst compound, LEED-Auger measurements were made on UO_2 (~ 100) vicinal surfaces. These (~ 100) vicinal surfaces were shown to decompose irreversibly into lower index facets, including prominent (100) facets, at temperatures below those needed for creation of lowest index faceting on (~ 111) vicinal surfaces. LEED examination of fully faceted surfaces from both types of UO_2 vicinal cuts did not show evidence of cyclopropane or propene chemisorption. The existing LEED-Auger system was modified to allow catalytic reactions at $\leq 10^{-3}$ torr. A sample holder, specifically designed for catalysis measurements in the modified system, was tested while examining single crystals of CoO and Cr_2O_3 . Extensive LEED-Auger measurements were made on CoO in vacuo and in the presence of light hydrocarbons and alcohols plus H_2O , NO , and NH_3 . No chemisorptive behavior was observed except with H_2O in the presence of the electron beam. Although only examined briefly, the Cr_2O_3 was remarkable for the sharp LEED features obtained prior to any surface treatment in the vacuum system.

I. INTRODUCTION

The New Research Initiatives Program (NRIP) project on catalysis in Group CMB-8 has made substantial progress towards performing the first basic in situ

experimental studies of heterogeneous catalysis on solid compound surfaces in a LEED-Auger system.

During the past 15 years a number of valuable techniques have been developed which permit detailed experimental analysis of the solid-gas interface. These analytical methods employ state-of-the-art vacuum technology to create an environment appropriate for surface examination via electrons, ions, photons, or other atomic scale probes. Some of these surface tools give information on the surface constituents or crystallography while others measure the electronic properties of the surface.

Group CMB-8 has been active in surface characterization through use of low energy electron diffraction (LEED),¹ Auger electron spectroscopy (AES),² ion scattering spectroscopy (ISS),³ and photoemission spectroscopy (PES).⁴ Where single crystal material is under study, LEED is used for surface crystallographic measurements of the substrate and adsorbed foreign species. AES is primarily utilized to determine surface composition by analysis of well-defined Auger electron energies found in the secondary electron energy spectrum. ISS seeks the same type of information by energy measurement of ions scattered from a surface. In addition to composition measurements, PES records surface electronic properties by energy analysis of photoemitted electrons. The NRIP project on catalysis in Group CMB-8 has focussed on using a LEED-Auger system to characterize surface parameters important in heterogeneous catalysis on various solid compounds.

A substantial amount of basic research in surface characterization of catalysts has and is being done at the Lawrence Berkeley Laboratory by Prof. Gabor A. Somorjai and his colleagues. Most of this effort has been directed towards understanding catalysis on single-crystal configurations of clean platinum.⁵ Their research has correlated catalytic activity with the presence of surface defects in the form of simple steps and steps with kinks. To date^{6, 7} they have shown that simple steps are responsible for H-H and C-H bond breaking while kink sites have the added ability of breaking C-C bonds. The experimentation has produced information on carbon overlayer structures, or template structures, that are a factor in controlling catalytic activity. Their work has detailed the stability and restructuring properties of various high-index Pt surfaces in the presence of oxygen or carbon.⁸ With the exception of a few stable surfaces, most high-index planes were altered by changing the environment. Extrapolating these results to dispersed particles of Pt, the stable surfaces were thought to

be the dominant catalyst surface structures in hydrocarbon catalysis. Most of the research in Somorjai's group has been accomplished using LEED and AES supported by mass spectrometer analysis of catalytic reaction products at pressures $\leq 10^{-3}$ torr. At these pressures the ultra-high vacuum system housing the experimental probes serves as the catalytic reaction vessel. In the last several years, Somorjai has modified or built several systems which incorporate both ultra-high vacuum and atmospheric pressure features.^{9, 10} Such a state-of-the-art system allows ultra-high vacuum characterization of a catalyst surface (i.e., AES, LEED, or thermal desorption) before and after running a catalytic reaction at atmospheric pressure. This apparatus has been used to analyze the hydrocarbon products formed by CO-H_2 and $\text{CO}_2\text{-H}_2$ reactions over polycrystalline rhodium at 700 torr.¹¹

In a study of the catalytic oxidation of CO on stepped platinum surfaces, Hopster et al.¹² have reported the interrelation of step density and O_2/CO pressure ratio. Using LEED and AES measurements at pressures $\leq 10^{-6}$ torr, they found values for CO reaction probability, oxygen coverage, and oxygen sticking coefficient. Their results indicate that surface defects in the form of steps may increase or decrease the catalytic oxidation of CO relative to a (111) platinum surface depending on the reaction conditions. Additionally, they have shown that the oxygen sticking coefficient for coverages between 0.02 and 0.10 monolayer increases exponentially with step concentration — requiring a nonlocal explanation for adsorption on a stepped surface.

The CMB-8 catalysis project on solid compounds parallels the ideas and techniques behind Somorjai's catalysis research program on metals. However, the effort has concentrated strictly on in situ catalysis measurements at $\leq 10^{-3}$ torr in a modified LEED-Augur system. Catalytic properties on solid compounds have not previously been examined in this manner as the difficulty of obtaining easily interpretable results far exceeds that for similar measurements on a pure metal. This is a consequence of the addition of a second major bulk constituent where, undoubtedly, the thermodynamic and electronic properties of the compound in the near surface region differ markedly from those of the bulk.

In the past Group CMB-8 has been involved in surface measurements on actinide elements, their alloys, and compounds. A considerable effort has been expended determining the surface composition and crystallography of single crystal UO_2 . Through use of LEED, Ellis and Schwoebel¹³ demonstrated that the $\text{UO}_2(553)$ surface could be ordered to form a repeating sequence of steps of minimum height.

In this first analysis of diffraction produced by a stepped surface, they suggested that such defect surface structures be examined for catalytic effects. The NRIP project on catalysis represents the initial attempt to pursue this suggestion in Group CMB-8. Since the pioneering experiment on stepped surfaces, Ellis has used LEED to analyze other UO_2 (~111) vicinal surfaces of more complex crystallographic content.¹⁴ Analogous information from UO_2 single-crystal surface models has been gained through application of laser transforms.^{14, 15, 16} Because such a vast amount of information on step structured surfaces of single-crystal UO_2 is available in CMB-8, this material was a natural selection as one of the compounds to be included in this project. In addition, because of the relevance of 3d oxides to commercial processes, single-crystal materials of cobaltous oxide (CoO) and chromia (Cr_2O_3) were incorporated in the study.

The NRIP catalysis studies program in CMB-8 has developed in three stages. First, to further augment understanding of possible catalyst surfaces, an examination of UO_2 (~100) vicinal surfaces was undertaken in the existing LEED-Auger vacuum system. Second, the LEED-Auger vacuum chamber was modified so that it could be used as a catalytic reaction vessel at pressures $\lesssim 10^{-3}$ torr. Third, single crystal samples of UO_2 , CoO , and Cr_2O_3 were examined in the modified LEED-Auger system. The remainder of this report will treat these three stages in some detail.

II. STUDY OF UO_2 (~100) VICINAL SURFACES

A. Step Surface Crystallography and Its Measurement

Measurements were made on two types of high-index surfaces vicinal to the UO_2 (100) face. In a perfectly ordered condition, these two classes of surfaces consist either of uniform arrangements of simple steps (terrace-ledge array, TL) or of steps with kinks at regular intervals (terrace-ledge-kink array, TLK). The drawings and hard-sphere models of Fig. 1 demonstrate the two types of UO_2 (~100) vicinal surfaces. Removing the kink site atoms from the TLK models of Figs. 1C and 1D reduces them to the (711) TL array of Fig. 1A and the (510) TL array of Fig. 1B, respectively. Note that in the hard-sphere models where the oxygen atoms are included, the ledges appear as {111} planes for the (711) surface and as {110} planes for the (510) surface. If the kink site atoms are included, as shown in Figs. 1C and 1D, the topmost ledges in the TLK arrays exhibit two kinds of possible kink structures. For viewing clarity the outermost oxygen layer has been omitted in both hard-sphere models. Of course, a real surface is

Fig. 1

- A. Idealized drawing of a $\text{UO}_2(711)$ stepped surface. Oxygen atoms have been omitted. Ledges are drawn as $\{111\}$ planes.
 - B. Idealized drawing of a $\text{UO}_2(510)$ stepped surface. Oxygen atoms have been omitted. Ledges are drawn as $\{100\}$ planes.
 - C. Hard-sphere model showing a possible $\text{UO}_2(\sim 100)$ vicinal TLK arrangement produced by adding kink-site atoms to the (711) TL surface. (711) ledges appear as $\{111\}$ planes.
 - D. Hard-sphere model showing a possible $\text{UO}_2(\sim 111)$ vicinal TLK arrangement produced by adding kink-site atoms to the (510) TL surface. (510) ledges appear as $\{110\}$ planes.
- Large dark spheres are oxygen atoms. Large grey spheres are kink-site oxygen atoms. Small white spheres are uranium atoms.

inhomogeneous to the extent that it will statistically contain a number of random deviations or mistakes from such ideal representations. This statistical content is a function of overall surface uniformity, cleanliness, and previous treatment.

If a monoenergetic beam of electrons is incident on a single-crystal surface, elastic diffraction will result when the difference between the scattered and incident electron wave vectors, $\vec{k}_f - \vec{k}_i$, where $|\vec{k}_f| = |\vec{k}_i|$, is equal to a surface reciprocal lattice vector.¹ For a simple one-dimensional chain of interatomic spacing "a," diffraction for normal incidence obeys the Bragg condition

$$a \sin \Theta = m\lambda , \quad (1)$$

where Θ is the scattering angle, λ is the electron wavelength, and m is an integer. The electron wavelength is given nonrelativistically by

$$\lambda = (150/\text{eV})^{1/2} , \quad (2)$$

where eV is the electron's kinetic energy in electron volts. The term low-energy electron diffraction or its acronym LEED is applied to an electron energy range between 10 and 500 eV. LEED readily yields information on surface symmetry and interatomic spacings. However, determination of exact atomic locations on the surface via LEED data is much more difficult and the solution of this problem is still the object of much attention.¹⁷

A typical LEED experimental setup is schematically represented by Fig. 2. The electron gun, located within the LEED optics, generates a focussed beam of electrons of approximately 0.5-eV half-width. The focussed electrons travel down the drift tube and strike the sample at ground potential. Electrons inelastically scattered into the LEED optics are rejected by two retarding grids so that only the back diffracted elastic electrons are imaged by the fluorescent screen subtending a solid angle behind the drift tube. Thus, for example, a clean, well-ordered (100) fcc single-crystal surface will produce a fourfold spot pattern on the screen that is easily seen by an observer through the vacuum viewport. The substrate spots in the diffraction pattern are indexed using integers. In the inelastic or Auger mode of operation, the two inner grids are modulated and ramped electronically while the fluorescent screen serves as the collector for a phase sensitive detection configuration used to measure the electron energy spectrum. All surface measurements are usually done under ultra-high vacuum conditions to preserve the state of the surface during the course of data acquisition.

Fig. 3

Two dimensional TL model and the kinematic LEED intensity, $I(\theta)$, from its terraces and steps. $I(\theta)$ is calculated from the terrace and step factors of Eq. (3), taken from Henzler¹⁸ where $N=6$, $|\vec{a}| = 3.46 \text{ \AA}$, $|\vec{d}| = 3.25 \text{ \AA}$, $|\vec{g}| = 1/3 |\vec{a}|$, and $\lambda = 1.45 \text{ \AA}$ (incident energy = 71 eV). A doublet voltage condition is indicated near $\theta = 0^\circ$. Arrows show direction in which diffraction features move as λ is decreased.

diffraction features move through one another as the energy is changed and give rise to a variety of spot configurations. Two simple diffraction conditions are evident. First, when the maxima of the two factors of Eq. (3) coincide, one intense spot is observed at the location of the low index integral spot. For the (00) terrace spot

$$V_{00} = 150 s^2 / 4d^2 \quad (4)$$

where V_{00} is the incident electron energy and "s" is an integer. Second, a diffraction doublet is observed when two delta functions are symmetrically located about a low index maximum, as is the case for $I(\theta)$ near (00) in Fig. 3. The angular separation of the doublets in the vicinity of $\theta = 0$ is given by

$$\Delta\theta = \frac{\lambda}{(N-1)a + g} \quad (5)$$

These types of simple kinematical calculations include only single scattering events and no electron penetration below the surface layer. A very complicated dynamical calculation of the scattering which includes multiple events, electron penetration into the solid, and electron attenuation from inelastic events, would be necessary to faithfully reproduce the intensity variation of the diffraction as a function of incident electron energy. While the kinematical calculation gives information on the allowed diffraction features, only a poor first-order approximation is made regarding the diffracted intensities.

In general, the LEED pattern obtained from an ordered array of steps is characterized by a splitting of the integral order spots associated with the terraces forming the steps. Singlets, doublets, and multiplets aligned in a

direction normal to the average ledge direction may appear as a function of incident energy near any of the integral order spot positions. With increasing energy the diffraction spots from a step array move so that the pattern as a whole converges toward specular reflection for the high-index surface in question. Determination of the angle relating this specular reflection to that for a known direction allows indexing of the stepped surface. The following work applies these ideas pictorially by photographing LEED patterns from stepped surfaces with variation in incident electron energy. The streak or convergence photo obtained readily lends itself to interpretation using the ideas presented in Fig. 3.

Kinematical calculation of the diffraction from a three-dimensional (553) surface model has been successfully done by Ellis and Schwoebel.¹³ However, for more complicated surfaces and, to be sure, for those including some disorder, the calculation would involve a great deal of time. As previously mentioned, optical simulation of such complex systems has been successfully employed by Ellis^{14,15,16} to gain some general insights into their diffraction features. As described by Ellis¹⁴ for both ordered and disordered stepped UO_2 surfaces, the topmost uranium atoms are projected onto a low index plane to form a two-dimensional array. A small grating is made by photographing the array after which laser light is passed through the grating and the diffraction then imaged on a screen. Although the voltage dependence of the diffracted beam positions and intensities is lost, the main features of the electron diffraction are contained in the analogous optical simulation. Variation of the electron energy should produce the diffraction features seen in the analogous optical pattern. The grating used for optical simulation of a UO_2 TLK surface, vicinal to the (100) plane, is shown in Fig. 4A. The optical diffraction pattern from this grating is reproduced in Fig. 4B. Note that the direction defined by the intense doublets is normal to the average ledge direction indicated on the grating. Ellis¹⁴ has shown that the addition of TLK disorder to the two-dimensional surface model increases the background and washes out all but the most intense diffraction features.

B. Samples and Apparatus

A four grid, fluorescent display LEED-Auger system was used to study three samples. Two of the samples, cut to expose (100) vicinal faces, were being examined for the first time. The third had been previously used in the UO_2 (~ 111) vicinal experiment.¹⁴ The UO_2 (~ 100) vicinal faces were cut at a polar angle, β ,

A

B

Fig. 4

- A. Optical grating used to simulate a UC_2 TLK surface vicinal to the (100) plane.
- B. Optical diffraction pattern produced by the grating in (A). Arrows indicate intense doublet features near lowest order terrace beams.

of 11.5° from the (100) surface and at the azimuthal angles, α , indicated in Fig. 5. As noted in the table of Fig. 5, two of these surfaces are very nearly equivalent to (711) and (510) planes. If the uranium atoms in the topmost layers of well-ordered (711) and (510) stepped surfaces are projected onto the (100) plane, arrays like those of Figs. 6A and 6C are obtained. Similar projections of well ordered TLK surfaces E and F, shown in Figs. 6B and 6D, give a clear picture of the sequence of kinks present in each high-index face. These latter two projections show an average ledge direction of $\langle 210 \rangle$ and $\langle 510 \rangle$ for surfaces E and F, respectively. Sample one contained three distinct faces: (711), E, and a (100) reference. Sample two contained four distinct faces: (711), (510), F, and a (100) reference. The third sample was composed of a (111) reference face and three TLK faces (A, B, D) cut at similar polar angles (14.5° , 13° , 13°) from the (100) face, and having azimuthal angles (30° , 16° , 47°) about the [111] pole that spanned the 60° angle measured from the $\langle 553 \rangle$ to the $\langle 311 \rangle$ pole projection on the (111) plane. (See Ref. 14 for more crystallographic detail). This last sample was repolished by hand and undoubtedly the faces were not as planar or uniform as when first examined.

After cutting and coarse grinding to give the above sample configurations, the various surfaces were fine polished in 1- μ Struers diamond paste. The remaining mechanically disturbed layers were removed by etching at 285°C in HF vapor, followed by 1.5-minute immersion in a 0.2M-solution of HNO_3 . Each sample

Fig. 5

Crystallographic pole diagram showing the five surfaces examined, where α and β are the azimuthal and polar angles defined by the inset. The arrows pointing to [100] and <311> from <711>, <510>, E, and F indicate the final facet configurations as discussed in the test.

was mounted on a stainless steel holder by means of a Pt mesh and placed in the vacuum chamber immediately after the final chemical etching. All face orientations were verified within $\pm 1^\circ$ by using standard Laue x-ray techniques.

The holder-plus-sample assembly could be heated in vacuum by an arrangement of cathode heaters suspended within the holder. Temperature measurements were made via a Pt - 10%Rh-Pt thermocouple spot welded to the holder. Unknown thermal contact between the sample and holder limited the accuracy of sample temperature determination to no better than $\sim 50^\circ\text{C}$. Prior to experimental measurements, but following bakeout, the vacuum chamber typically reached pressures $\leq 10^{-10}$ torr. Composition of the base pressure gas and purity of intentionally

Fig. 6

Projections of various stepped UO_2 surfaces onto the (100) plane. Successive (100) terraces are alternately dots (•) and circles (◦). Only the topmost uranium atoms have been projected.

- A. TL, (711)
- B. TLK, surface E
- C. TL, (510)
- D. TLK, surface F

introduced gases, i.e., Ar or O₂, was monitored using a quadrupole residual gas analyzer. Laser transform modeling was accomplished by using the previously described apparatus.¹⁵

C. Results

Following vacuum chamber bakeout, AES measurements on the UO₂ surfaces indicated a significant amount of carbon surface contamination. Some chlorine, calcium, and sulfur impurity was also evident at this stage of the experiment. For these surface conditions the LEED patterns were barely visible over a bright background produced by diffuse electron scattering. Argon ion bombardment at energies ≤ 200 eV was used to eliminate surface impurities. (Unlike the previous study,¹⁴ surface impurities could not be removed by just heating the samples to $< 500^\circ\text{C}$ in $\sim 10^{-6}$ torr O₂). The imbedded argon was largely desorbed from the samples after anneal to about 400°C . For all the subsequent LEED results, AES showed no significant surface contamination.

1. The UO₂(100) Surface. The UO₂(100) surface did not facet at temperatures up to 950°C . A well-ordered, clean UO₂(100) surface gave the spot pattern of Fig. 7A. The pattern is a $c(2 \times 2)$ where the $(\pm n/2 \pm n/2)$ spots, n odd, are on the average much weaker than the other half-order features. The $(\pm 1/2 \pm 1/2)$ spots were visible only at incident energies below about 50 eV. All the half-order spots could be eliminated from the pattern by ion bombardment. The $c(2 \times 2)$ surface condition was difficult to analyze because the half-order spots were affected by the incident electron beam. For incident energies near 100 eV, the $c(2 \times 2)$ pattern degraded in intensity until, after a period of hours beam time in the absence of gas phase O₂, a variety of new nonintegral order features were observed. A sharp $c(4 \times 4)$ pattern, shown in Fig. 7B, was first formed under the electron beam. This was followed by the addition of more extra spots and the gradual formation of streaky crosses as shown in Fig. 7C. Such pattern changes occurred much more rapidly during AES measurements, where larger incident current and energy (1 keV) were employed than in the LEED analysis. AES indicated no significant compositional effects during the course of the beam induced surface changes. The $c(2 \times 2)$ spot pattern could be regenerated by heating the sample for a sufficiently long time at $\geq 700^\circ\text{C}$ and $\sim 10^{-9}$ torr pressure in the absence of the electron beam. These results agree with an earlier incomplete study of UO₂(100).¹⁹

2. The UO₂(~ 100) Vicinal Surfaces. As mentioned above, the four UO₂(~ 100) vicinal surfaces examined in this work were distributed on two separate samples.

A

B

Fig. 7

- A. c(2x2) spot pattern from the clean $\text{UO}_2(100)$ surface at an incident energy of 124 eV.
- B. Electron beam induced c(4x4) spot pattern from the $\text{UO}_2(100)$ surface at an incident energy of 57 eV. Missing spots visible at other energies.
- C. Electron beam induced LEED pattern from the $\text{UO}_2(100)$ surface at an incident energy of 57 eV. More beam exposure than photo B.

C

Each sample was analyzed in a separate set of measurements and in both cases care was taken to observe the ordering-faceting properties after increasing the temperature in increments of $50^\circ - 100^\circ\text{C}$.

a. Sample One: TL (711) and TLK surface E. After sample one was heated at $<500^\circ\text{C}$ in 10^{-6} torr of O_2 , the clean (711) surface produced the spot pattern of Fig. 8A. Note that the doublet energy condition for an ordered (711) face is evident for diffraction near several of the (100) integral spot positions. The photograph of Fig. 8B shows the (711) diffraction pattern during the course of linearly varying the incident electron energy. The streaks produced by the motion of the diffraction spots converge to the specular reflection point for the surface. The angle between this convergence point and the drift tube, θ_s , as

A

B

Fig. 8

- A. Spot pattern from the ordered $\text{UO}_2(711)$ surface at an incident energy of 124 eV. Arrows indicate doublet energy condition near (20) and (11) terrace spots.
- B. Convergence photo obtained from the ordered $\text{UO}_2(711)$ surface as the incident energy was swept from 100 to 160 eV. Incident electron beam normal to (100) face. "x" indicates point of convergence on fluorescent screen.

measured from the sample position, is twice the polar angle, β , listed in the table of Fig. 5. Prior to measuring these angles the (100) surface was aligned normal to the incident electron beam. The sample was then translated normal to the incident beam until the desired vicinal surface was located. The angular positions on the fluorescent screen were calibrated from the position of the (00) spot for known rotations of the (100) surface relative to the incident electron beam. As shown in Fig. 9A, heating the (711) surface above 600°C in 10^{-6} torr O_2 produced diffraction features from two types of facets. For this surface condition the spot convergence photo of Fig. 9B gives values of β indicating the presence of (311) and (100) faceting. This facet array, indicated by the solid arrows pointing to $[100]$ and $\langle 311 \rangle$ from $\langle 711 \rangle$ in Fig. 5, was the most ordered surface rearrangement observed during the course of the experiments on the (100) vicinal surfaces.

After heating the sample at $<500^\circ\text{C}$ in 10^{-6} torr O_2 , LEED measurements on TLK surface E showed an incomplete ordering of the closely spaced doublets shown in the photo of Fig. 10A. A convergence photo from this surface indicated a specular reflection consistent with the originally prepared surface. Further heating to $<600^\circ\text{C}$ introduced (100) facet features which could be identified

A

B

Fig. 5

- A. Spot pattern obtained from the (711) prepared surface at the final facet stage. Incident energy is 91 eV. Nonindexed prominent spots adjacent to ($0\bar{1}$) spot are from (311) faceting.
- B. Convergence photo obtained from fully faceted (711) prepared surface as the incident energy was swept from 92 to 146 eV. Incident electron beam normal to (100) face. "x" indicates point of convergence from (311) facets on fluorescent screen. "+" indicates point of convergence (drift tube) from (100) facets.

either by translating the sample under the incident electron beam from surface E to the (100) or by taking a convergence photo. Heating the sample above 600°C produced additional, poorly defined diffraction features indicating the presence of two sets of (311) facets. As shown by comparing Fig. 9A with Fig. 10B, the spacing and energy dependence of the latter diffraction streaks closely paralleled those seen from the ordered (311) facets of the (711) prepared face. The (311) faceting which gave the most intense diffraction features from surface E is indicated by the solid arrow pointing to $\langle 311 \rangle$ from E in Fig. 5. The dashed arrow from E in Fig. 5 indicates the (311) facets associated with the less intense diffraction features. The LEED patterns from surface E were generally quite streaky. Both TL (711) and TLK surface E showed no further obvious changes when heated to $\sim 750^\circ\text{C}$.

b. Sample Two: TL (711), TL (510), and TLK surface F. Following argon ion bombardment and anneal at $\leq 400^\circ\text{C}$ for several hours in $\sim 10^{-6}$ torr O_2 , the various faces of sample two produced vague doublets having the orientation and specular convergence properties of the prepared faces. The ordering was not as

A

B

Fig. 10

- A. Sharpest spot pattern obtained from TLK surface E prior to faceting. Incident energy is 75 eV. Arrow indicates doublet energy condition near (11) spot location.
- B. Spot pattern obtained from TLK surface E at the final facet stage. Incident energy is 90 eV. (100) facet spots are indexed. When compared to similar features in Fig. 9A, the streaky features adjacent the (10) spot indicate diffraction from a poorly ordered primary set of (311) facets oriented perpendicular to those of Fig. 9A. The secondary (311) features adjacent to the (01) spot are too weak to be seen in the photo.

well developed as that of the (711) surface of sample one. When sample two was heated for 24 hours in $\sim 10^{-9}$ torr vacuum at $\sim 450^\circ\text{C}$, poorly ordered facet-like diffraction features were observed and further heating to $\sim 500^\circ\text{C}$ gave LEED results indicating some (100) content on each of the three (100) vicinal surfaces. Heating to higher temperatures in 10^{-6} torr O_2 again produced the ordered (311) plus (100) facet configuration on the (711) prepared face. This faceting was stable in $\sim 10^{-8}$ torr vacuum for sample temperatures up to 950°C (higher temperature than was possible with sample one due to a different heater arrangement).

For the (510) surface and temperatures between 500 and 800°C , fairly sharp diffraction features were observed in addition to those obviously associated with (100) faceting. Overlap of the former features with the (100) spots in a convergence photo obscured specular reflection. However, two sets of closely spaced but distinct non-(100) spots resulted from exposure of a photo at 90 and 117 eV. Extending a line through these doublet pairs indicated specular reflection very near that for the (410) plane. Heating above 800°C degraded these non-(100) diffraction features and produced streaks indicative of (311) faceting.

The spacing and energy dependence of these diffraction streaks (shown in Fig. 11A) closely resembled that observed from the (311) faceting of the (711) prepared surface (see Fig. 9A). As indicated by the streak intensity in Fig. 11A, this latter faceting occurred in equal amounts in the two perpendicular directions designated by the solid arrows pointing to $\langle 311 \rangle$ poles from the $\langle 510 \rangle$ in Fig. 5.

Between 600 and 800°C, TLK surface F yielded diffraction that, with the exception of some additional streaking, was similar to that seen on the (510) prepared face for this temperature range. As attested to by the LEED photos of Figs. 9A and 11B, heating above 800°C again gave poorly defined diffraction features showing the presence of (311) faceting. However, unlike those seen from the (510) prepared surface, one set of diffraction streaks was more intense than the set seen at 90°. The solid arrow pointing to $\langle 311 \rangle$ from F in Fig. 5 indicates the (311) facets giving the more intense LEED features, while the dashed arrow from F indicates the secondary set of (311) facets associated with the less intense diffraction.

A

B

Fig. 11

- A. Spot pattern obtained from (510) prepared surface at the final facet stage. Incident energy is 91 eV. (100) facet spots are indexed. When compared to similar features in Fig. 9A, the streaky features adjacent to the (10) and (0 $\bar{1}$) spots indicate diffraction from two sets of poorly ordered (311) facets oriented perpendicular to one another.
- B. Spot pattern obtained from TLK surface F at the final facet stage. Incident energy is 91 eV. (100) facet spots are indexed. When compared to similar features in Fig. 9A, the streaky features adjacent to the (10) spot indicate diffraction from a poorly ordered primary set of (311) facets oriented perpendicular to those of Fig. 9A. Similar secondary (311) features are adjacent to the (0 $\bar{1}$) spot.

AES spectra from the various surfaces of these two samples at each stage of the experiment did not differ significantly. The $c(2 \times 2)$ half order diffraction features from the nonfaceted vicinal cuts were elongated in a direction parallel to that defined by the observed doublets. (100) faceting enhanced the sharpness and intensity of these half order diffraction features.

3. The $\text{UO}_2(\sim 111)$ Vicinal Surfaces. The $\text{UO}_2(\sim 111)$ vicinal surfaces were included in this study to determine the effect that ion bombardment would have on their ordering and faceting properties. Ion bombardment was not used as a cleaning technique in the previous measurements on these surfaces.¹⁴ The LEED results obtained on the $\text{UO}_2(\sim 111)$ vicinal surfaces after argon ion bombardment as a function of temperature and oxygen treatment essentially agree with the past work. However, several minor variations in the diffraction features were observed which deserve mention.

As shown in Fig. 12A, a complete half-order spot pattern was seen on the (111) surface. A half order pattern such as this was found after anneal near 700°C with or without O_2 in the gas phase. The pattern was degraded by the electron beam. Each of the three TLK surfaces exhibited half-order features - but at only one-third of the (111) half-order positions were they intense enough to be clearly resolvable as doublets. The remaining two-thirds half-order

A

B

Fig. 12

- A. Half-order spot pattern obtained from clean $\text{UO}_2(111)$ surface. Incident energy is 88 eV.
- B. Split half-order spot pattern obtained from clean $\text{UO}_2(\sim 111)$ vicinal surface D (see Ref. 14). Incident energy is 102 eV. Short arrow points to $(1/2 \bar{1})$ doublet. Long arrow points to $(0\bar{1})$ doublet.

positions were occupied by poorly defined, dim intensity features. One example of such a pattern is shown in Fig. 12B for TLK surface D.

After annealing TLK surface A for one hour at 800°C in ultra high vacuum a triplet of split Bragg spots was photographed within the same angular spread as the doublets typically observed from this surface. These diffraction features are taken as evidence of an ordered array of double steps. At this stage in the measurements there was an obvious amount of (111) facet content on TLK surface D. The other two TLK surfaces may also have included some (111) faceting.

Neither the double stepping nor the (111) facet content was previously reported.¹⁴ However, the split half-order spots were previously seen in much weaker form.

D. Discussion

As stated above, the $\text{UO}_2(\sim 111)$ vicinal surfaces were included in this study to determine the effect that ion bombardment would have on their ordering and faceting properties. The results indicate that bombardment introduces no dramatic changes in their previously reported¹⁴ behavior. The ion bombarded $\text{UO}_2(\sim 111)$ vicinal surfaces exhibited ordering comparable to that of the previous study. Thus, it is deemed more likely that ion bombardment, used as a necessary cleaning procedure on the $\text{UO}_2(\sim 100)$ vicinal surfaces, was not the major cause for the disorder encountered with those surfaces. The (711) prepared face, with its rearrangement into (311) and (100) facets, was the only $\text{UO}_2(\sim 100)$ vicinal surface to exhibit sharp, easily interpretable diffraction features.

The previous study of $\text{UO}_2(\sim 111)$ vicinal surfaces¹⁴ reported intermediate faceting processes (i.e., rotating ledges) which could be reversed by heating in O_2 at reduced temperatures to recreate the diffraction conditions of the original stepped surface. For those vicinal surfaces, the growth of (111) facets was not observed at temperatures up to 900°C. In the present work, where the $\text{UO}_2(\sim 111)$ vicinal sample was less perfectly prepared than in the earlier measurements, a minor amount of (111) facet growth was indicated by the LEED patterns. The rotating ledge properties were reproduced. The $\{100\}$ vicinal surfaces showed a strong tendency to decompose directly to the nearby low index plane at temperatures much below 900°C. No intermediate facet stages were observed which were reversible under heat treatment in O_2 . However, it is possible that such effects were overlooked because of the large amount of disorder exhibited by the LEED patterns.

Well-defined ordering and final faceting on a stepped surface requires long range movement of a diffusing surface species. Such long range surface communication is evidently not the rule on the (100) vicinal surfaces where isolated microscopic surface rearrangement is prevalent. The fourfold (100) terraces, in contrast to the threefold (111) terraces, seem to act as surface diffusion barriers that limit long range surface communication while growing at the expense of intermediate faceting stages. The (311) facets have narrow terraces and thus permit better communication and more uniformity across the step arrangement. As was previously observed,¹⁴ the mobility and/or composition of the diffusing species on the (111) vicinal surfaces was definitely altered in the presence of O_2 to enable reversal of the intermediate faceting sequence. Possibly a three-fold uranium oxide molecule serves as the diffusing species which either is not readily produced or easily transported across the (100) terraces. Detailed analysis of these effects would require more knowledge of the origin of the half order structures, mostly likely due to oxygen, seen on the two types of terraces.

The preservation of macroscopic surface orientation imposes qualitative restrictions on the facet composition of a surface. Figure 13A demonstrates that the appearance of (100) facets on the (711) surface requires steep interconnecting stepped surfaces. These interconnecting regions obviously need not exhibit the order or perfect (311) content of that shown in the drawing. Fig. 13B represents a two-dimensional projection of a possible (100), TL, TLK facet

Fig. 13

- A. Upper drawing: side view of (711) stepped surface, $\beta_1 = 11.4^\circ$.
Lower drawing: side view of (100) and (311) facets obtained from the (711) prepared surface, $\beta_2 = 25.2^\circ$.
- B. Two-dimensional projection of a possible facet configuration from TLK surface E. TL and TLK regions are not necessarily uniform.

mixture which could yield the final diffraction results obtained from TLK surface E. In the model, the (100) facets are joined by regions of TL (oriented in two perpendicular directions) and TLK to preserve the macroscopic surface orientation. A number of poorly developed (311) regions must be present to produce the streaky (311) diffraction features seen from surface E. An assortment of other TL and TLK regions are most likely present which also produce poorly defined diffraction features.

The previously reported half-order LEED pattern from the $\text{UO}_2(111)$ surface was attributed to a $p(2 \times 2)$ overlayer structure of oxygen. Little attention was paid to split half-order spots seen with stepped surfaces due to very weak intensity. However, in the present work these split half-orders were brighter and allowed a more detailed interpretation. The half-order spot pattern of Fig. 12A can result from a $p(2 \times 2)$ structure or a (2×1) structure of three equivalently oriented domains. The ambiguity between these two surface structures appears to be removed in the presence of a stepped surface. Overlooking the obvious intensity effects of doublet generation, Fig. 12B shows that the relative intensity of the half-order doublets differs considerably from the threefold intensity character expected from a $p(2 \times 2)$ structure. As seen in Fig. 12B two-thirds of the half order doublets that would be anticipated with the $p(2 \times 2)$ structure are of extremely poor quality and very weak in intensity. A mismatch between the overlayer structures on the various terraces would decrease the quality of all the half order doublets from a $p(2 \times 2)$ arrangement. Apparently the introduction of steps via a (~ 111) TLK surface resulted in preferential selection of one of the three available (2×1) domains that precluded prominent ordered growth of the other two. The dominant split half-order spots of Fig. 12B can be explained by the (2×1) overlayer mesh on surface TLK D of Fig. 14. Each of the other two vicinal (111) TLK surfaces exhibited a set of intense split half-orders that correspond to (2×1) overlayer growth along equivalent crystallographic directions (also shown in Fig. 14). The vague half order features of Fig. 12B, could be derived from a minor amount of (111) faceting which, as seen in Fig. 12A, yields all three sets of (2×1) domains. Possibly random nonuniformities on the (111) face, in the form of simple steps or steps with kinks, serve as nucleation centers for approximately equal populations of the three (2×1) domains. The resultant half order pattern could not be distinguished from that of a $p(2 \times 2)$ overlayer structure without detailed intensity analysis.

Fig. 14

Surface model showing orientation of dominant (2x1) unit mesh relative to the average ledge direction for the $\text{UO}_2(\sim 111)$ vicinal surfaces of the inset (see Ref. 14). Uranium atoms are located at triangle corners. Dots (•) indicate (2x1) periodicity.

vicinal surfaces as compared to $\text{UO}_2(\sim 111)$ vicinal surfaces reflects a difference in the oxygen bonding properties of the two fluorite materials. Thorium forms a narrowly stoichiometric oxide while uranium not only exhibits several valence states, but also forms hyper and hypostoichiometric UO_2 via defect sites. The surface species responsible for the long-range communication between steps on such oxide surfaces is apparently more readily formed where metal atoms of multiple valence and oxygen defect structures are a possibility.

A summary of this work on $\text{UO}_2(\sim 100)$ vicinal surfaces was presented by W. P. Ellis and T. N. Taylor at the International Conference on Colloids and Surfaces, ACS and the IUPAC, San Juan, Puerto Rico, 21-25 June 1976, under the title: "Configurations of Terrace - Ledge - Kink Arrays: LEED-Auger Studies of $\text{UO}_2(\sim 100)$ Vicinal Surfaces." A manuscript relating in detail the $\text{UO}_2(\sim 100)$ vicinal surface behavior has been prepared for submission to the journal "Surface Science."

Although the ordering and faceting diffraction features of $\text{UO}_2(\sim 100)$ vicinal surfaces are of poorer quality than those observed from $\text{UO}_2(\sim 111)$ vicinal surfaces, they are much more evident than those seen from $\text{ThO}_2(\sim 111)$ vicinal surfaces. In a similar LEED examination of the ordering and faceting properties of $\text{ThO}_2(\sim 111)$ vicinal faces,²⁰ we observed no definitive diffraction beam splitting from the originally prepared surfaces. Faceting was not evident via LEED in the presence or absence of gas phase oxygen at temperatures up to 900°C. (AES examination of these surfaces after heating in oxygen showed only Th and O peaks - where the two Th peaks between 230 and 250 eV showed an extreme form of the relative peak intensities reported for oxygen chemisorption on single crystal thorium.²¹) The ordering and faceting behavior of $\text{ThO}_2(\sim 111)$

III. MODIFICATIONS OF THE LEED-AUGER VACUUM CHAMBER FOR CATALYSIS STUDIES

As mentioned in the introduction section, the NRIP project on catalysis in CMB-8 has been concerned only with catalytic reactions at $\lesssim 10^{-3}$ torr using a LEED-Auger vacuum chamber as the reaction vessel. The apparatus, as it was employed to study the $\text{UO}_2(\sim 100)$ vicinal surfaces, required modifications for catalysis measurements. A schematic of the LEED-Auger system as modified is drawn in Fig. 15. The reaction volume includes the LEED-Auger instrumentation, ionization gauge (IG), quadrupole residual gas analyzer (RGA), and ion bombardment gun. Reaction gases may be introduced into the reaction chamber through separate leak valves from high-pressure gas lines. A stainless steel capillary tube has been welded to the low-pressure port of one of the leak valves. With the tube directed at the sample (catalyst material), the effective pressure of the reaction gas at the sample surface is larger than the ambient pressure of the vacuum chamber.²² Thus, for experimental situations where a small amount of reaction gas is required to make an observation, the vacuum chamber need not be saturated with the gas—which in some instances involves a substantial pump down time for attainment of ultra-high vacuum pressures. The sample can be positioned in front of the capillary tube and in line of sight of the RGA while still allowing LEED or AES

measurements.

Prior to its conversion to a catalysis reaction vessel, the LEED-Auger system had only been utilized in ultra-high vacuum applications where easily pumped elemental gases were introduced at low pressures. Substantial VacIon[®]* pump contamination resulted only during pump-down and bakeout when atmospheric gases and cleaning vapors dominated the gas composition. Pumping relatively large amounts of organic gases would adversely affect the performance of the VacIon[®] pump and result in a higher system base pressure.

Fig. 15

Schematic representation of LEED-Auger vacuum system as modified for use in the catalysis studies.

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To meet the dual requirements for catalytic reactions at up to 10^{-3} torr plus LEED-Auger surface characterization at ultra-high vacuum pressures, two important changes were made in the vacuum chamber, as shown in Fig. 15. First an all-metal gate valve was placed between the existing VacIor[®] pump and the experimental section of the vacuum chamber or reaction vessel. The gate valve is completely bakeable to ~225°C. Second, a liquid nitrogen trapped diffusion pump was attached to the reaction chamber. A 2-3/4-in. all-metal valve is used to separate the reaction vessel from the clean side of the trap. Optimum vacuum integrity was obtained from the diffusion pump (2-in. throat diam, water-cooled) by welding a 4-1/2-in. o.d. ConFlat[®]* Flange to the entrance port. By using Convalex[®]** (polyphenyl ether) pump oil and proper bakeout of the trap prior to liquid nitrogen filling, the volume above the trap and below the 2-3/4-in. valve can routinely be pumped to $\leq 2 \times 10^{-9}$ torr. With the gate valve closed and the 2-3/4-in. valve fully open, the diffusion pump station will hold the reaction chamber pressure $\leq 10^{-8}$ torr provided the chamber has been adequately baked. By closing the gate valve and opening the 2-3/4-in. valve to the diffusion pump, catalysis measurements at up to 10^{-3} torr can be made without impairing the performance of the VacIor[®] pumping station. By throttling or totally closing these valves, the reaction of interest can be done in a static or nearly static gas environment to prevent reaction products from being pumped below the detection limits of the RGA. LEED or AES examination of the catalyst can be accomplished at pressures in the 10^{-7} torr range or less. (The indirectly heated electron-emitting cathode is adversely affected at higher pressures by most reactant gases.)

The method used to heat the catalyst introduces a number of complications. Localized ohmic heating of a thin sample, a technique often applied to metals, is not feasible for the class of materials studied in this work. The presence of hot filaments, necessary for indirect heating or electron bombardment, must be eliminated from the reaction chamber to prevent introduction of spurious cracking and catalytic reactions. (Low-temperature filaments of thoriated iridium have been inserted into the ionization gauge and RGA.) In addition, the sample holder must be catalytically inactive while a portion of it is at the elevated temperatures required for catalysis on the attached solid compound. A unique sample holder assembly was designed and built specifically to overcome these problems. As pictured in Fig. 16, the assembly consists of a hollow tantalum tip and hollow stainless steel body joined by electron beam welds to a stainless steel-tantalum

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Fig. 16

Photo of sample holder assembly. Square tantalum tip face for mounting samples is located near the middle of the assembly. When placed in the modified LEED-Auger system, the assembly is suspended vertically from the reaction chamber manipulator.

explosively bonded ring. The sample under investigation is pressed onto the tip by a spot-welded tantalum clasp. The supporting body includes a Mini ConFlat[®] connection and a stainless steel tube extending behind and beyond the tip. The Mini ConFlat[®] Flange is centered on the tip axis at the top of the assembly and mates to an electrical feed-through used to supply power to a triad of cathode heaters suspended inside the tip. The extended length of tubing behind the tip is welded to a bellows which coils once around the tip axis before being terminated by a second Mini ConFlat[®] connector. The

whole sample holder assembly is suspended from the reaction chamber manipulator by a split-ring adapter fastened around the top Mini ConFlat[®]. When inserted in the reaction chamber, the tubing-bellows combination is coupled through a tubular ceramic isolator to an open-ended 2-3/4-in. flange fitting attached to a bottom port of the reaction chamber. Thus, the internal volume of the sample holder can be pumped independently of the reaction chamber via plumbing connections to the diffusion pump and/or an 8 liter per sec VacIon[®] pump. The position of the tip, with sample attached, can be adjusted with the manipulator until the sample is located at the center of the LEED optics. The bellows is flexible enough to allow ~180° rotation about the sample manipulator axis. The whole assembly can be electrically isolated from ground so that the sample can be placed at a negative potential during ion bombardment. Sample temperatures are measured via a W-26%Re-W thermocouple spot welded to the tip face opposite the sample.

Initial heating of the tantalum in the LEED-Auger or reaction chamber produced hydrogen outgassing sufficient to shut off the VacIon[®] pumps (pressures in excess of 10^{-3} torr). By slowly increasing the temperature of the tantalum and using just the diffusion pump, the outgassing rate was eventually decreased to an acceptable level. With VacIon[®] pumping, the tip was outgassed for about 80 hours at 750°C. At this stage the gases produced inside the sample holder assembly were easily handled by the 8 liter per second VacIon[®] pump. With the

tantalum tip heated to 600°C and the gate valve closed, the diffusion pumped base pressure of the reaction chamber was 2×10^{-8} torr. For these same conditions and the gate valve open to the large VacIor® pump, the base pressure of the reaction chamber was about 2×10^{-9} torr. Following degassing, RGA analysis of the gas phase showed an increase in hydrogen, carbon monoxide, and carbon dioxide with increase in tip temperature. The maximum possible tip temperature for the power source available is 820°C at 33 watts input (11.25 Vrms, 2.95 Arms).

Tantalum was selected as a tip material because it was thought likely to be more catalytically inert than other readily available and machinable metals. During study of CoO, a large propene product was thermally desorbed after exposure of the tip plus sample to isopropyl alcohol. No LEED changes were noted from the CoO after exposure to the alcohol and prior to heating. Apparently the tantalum tip, with a superficial oxide layer detectable by AES, dehydrated the alcohol. Such sample holder interference with catalysis product measurements can possibly be eliminated by properly coating the tip with gold.

IV. STUDY OF CoO, Cr₂O₃, AND UO₂ IN THE MODIFIED LEED-AUGER SYSTEM

As a first step towards understanding the catalysis of oxides, the surfaces of the materials involved in this study were characterized using the LEED-Auger instrumentation. This involved measurements on the surfaces following various sample treatments related to cleaning the surfaces or examining their reactivity to well-controlled gas environments below 10^{-3} torr. The latter interactions or chemisorption properties are quite vital in any analysis of catalytic phenomena. For a catalyst to evidence appreciable activity at least one component of the reaction gases should be chemisorbed²³ on the catalyst surface (binding energy ≥ 1 eV). Gas species that are bound less strongly will be present on the surface in negligible numbers due to rapid desorption and may not be detectable with LEED-Auger.

UO₂ being the exception, both CoO and Cr₂O₃ have been examined to a limited extent with modern surface analytical probes. In neither instance are there any reports of LEED done on single crystal samples of the materials. For the latter two oxide materials, the clean surface properties measured via the LEED-Auger instrumentation are a definite object of interest prior to any study of chemisorption, and thus, catalysis effects.

A. Examination of CoO

Taken as a whole, cobalt oxide materials - mixed and unmixed with other transition metal oxides and on various supports - display a great variety of catalytic chemistry. A significant amount of interest has been taken in the ability some of them have for removing organically bound sulfur from petroleum fractions (hydrodesulfurization most prominently using cobalt-molybdena-alumina) and for the purification of exhaust gases through oxidation/reduction of NO, CO, and other combustion related products. Previous phenomenological, i.e. kinetic, studies have been made on various catalyst materials containing CoO in order to analyze hydrogenation, dehydrogenation, and isomerization of hydrocarbons, and oxidation reactions involving, for instance, ammonia or alcohols. The following relates efforts made to characterize the chemisorption of various simple catalytically related gases when exposed to a CoO sample having pronounced single crystal structure.

Electron binding energies for CoO in polycrystalline form have been recorded in a number of x-ray photoelectron spectroscopy (XPS) studies.^{24, 25, 26} The valence band spectra was shown²⁵ to be composed of peaks derived from cobalt 3d levels, the oxygen 2p level, and multielectron excitations in that order proceeding from the fermi level to ~10 eV binding energy. In a study of thin CoO samples, Bakulin²⁷ et al. reported transmission electron energy losses of 7.2 and 21.3 eV. As previously noted, no LEED-Auger measurements are available in the literature. This is undoubtedly in part due to the insulating properties of CoO which can cause pronounced charging effects in the presence of an electron beam.

CoO exhibits the NaCl crystal structure formed by a f.c.c. space lattice and a Co-O atom basis where the metal atom and oxygen atom are separated by half the diagonal distance of the unit cube ($a_0 = 4.27 \text{ \AA}$). The (111) face is polar, i.e., the topmost layer of atoms is either Co or O, while the (100) face is non-polar, i.e., the topmost layer of atoms is equally populated with Co and O. The CoO sample analyzed in this study was an elliptically shaped wafer about 1 cm^2 on a side. The outer periphery of the sample was oriented to expose the (111) face while the center portion contained a number of randomly oriented crystallites. One edge of the sample was cleaved to expose the (100) face. The cleaved surface was approximately 10 percent as large as the (111) face. After cutting and orienting to within $\pm 1/2^\circ$, the (111) face was polished with successively finer grit until a 1- μ diamond paste was reached. Immediately prior to placement

in the LEED-Augur chamber, the sample was immersed in a 1:10 solution of phosphoric acid at room temperature for 65 seconds and rinsed sequentially in deionized water and ethanol. The sample was mounted on the tantalum holder assembly.

AES examination of the CoO sample following bakeout with the base pressure $\leq 5 \times 10^{-10}$ torr indicated, in addition to the bulk constituents, C and Cl surface impurities. No electron diffraction features were detectable over a bright background and, due to sample charging, LEED measurements were not possible below ~ 50 eV.

Because in the early stages of the experiment the wire lead to the tantalum tip unknowingly became disconnected from the heater core, where the feedthrough wires were attached, the actual sample potential was poorly defined. The heater core was still in marginal contact with the tantalum tip. With this state of affairs the sample was argon ion bombarded - the gas continuously flowing through a leak valve and into the diffusion pump. The applied acceleration potential was 200 volts. Following this treatment and prior to anneal, vague diffraction features were visible from the (111) and (100) surfaces. AES indicated significant S and C impurities. Heating to 600°C considerably reduced these two contaminants and introduced a noticeable Ca peak in the AES spectrum. Further heating up to 775°C also produced K segregation on the surface. Following anneal above 700°C , the (111) surface produced a diffuse three-fold diffraction pattern with a slight suggestion of half-order features. The (100) surface gave much sharper diffraction and, as shown on Fig. 17 for this stage of the experimentation, streaking and (2x1) half-order spots were often seen between the integral-order features. The composition of the (100) face was difficult to measure reliably with AES due to the narrowness and charging of the face. Large randomly oriented four-fold facets were detected in the multi-crystalline center portion of the sample. The LEED pattern from such a surface is shown in Fig. 18. The surface content of the center portion of the sample, measured via AES, did not differ significantly from that of the (111) periphery. Sample charging interfered with LEED measurements for incident energies ≤ 80 eV. Heating the sample at 820°C one hour in $\sim 10^{-6}$ torr oxygen produced no obvious LEED or AES changes.

After the disconnected wire lead had been found, the sample was properly ion bombarded at 250 eV (4×10^{-4} torr, 25°C , 1.25 hr.) by applying the acceleration potential directly to the tantalum tip via the spot welded thermocouple. (During the course of subsequent measurements the sample was also properly grounded through the thermocouple.) Following anneal in vacuo for about 4 hours at 820°C ,

Fig. 17

Spot pattern obtained from CoO(100) surface at a metered incident energy of 145 eV. Sample had been argon ion bombarded and heated as high as 775°C in vacuo. AES done on the major sample face indicated some S, K, C, and Ca surface impurities.

Fig. 18

Spot pattern obtained from a fourfold facet located in the multi-crystalline center portion of the CoO sample. Metered incident energy is 175 eV. Following treatment of Fig. 17, sample was heated at 820°C in vacuo and at 700°C in 10^{-6} torr of oxygen.

the half order LEED pattern of Fig. 19A was produced by the (111) surface. AES indicated significant K and Ca surface contamination. There was a small S impurity and no residual Cl or C. All these impurities were reduced to the noise level of the Auger spectrometer by heating the sample at 600°-700°C and simultaneously ion bombarding at 200 eV over a time period of hours. After heating the sample to 820°C in vacuo, the photograph of Fig. 19B was taken where AES at 1.5 KeV incident energy showed only Co and O. Immediately after cooling to near 25°C, LEED measurements were possible for several minutes at incident energies as low as 30 eV. However, continuous exposure to the electron beam eventually charged the sample and extinguished the LEED pattern for incident energies ≤ 100 eV. During the course of the remaining measurements on CoO, LEED pattern instabilities and AES noise associated with sample charging were greatly reduced by elevating the sample temperature to 100°-200°C. The LEED pattern from the (111) surface was still much more diffuse than that seen from the (100) face, where in the latter case streaking was visible between the integral order spots.

Electron energy loss measurements were also taken from the clean CoO surfaces. In making these inelastic measurements, the secondary electron energy spectrum, $N(E)$, is examined as a function of incident energy to locate peaks

Fig. 19

A

Half order spot pattern obtained from CoO(111) surface at a metered incident energy of 67 eV. Sample treatment and surface condition is described in text.

B

Integral-order spot pattern obtained from clean CoO(111) at a metered incident energy of 59 eV.

that are a fixed energy below the elastic peak. The LEED optics is used in the AES mode to detect $N(E)$ versus E . Loss peaks can often times be associated with atomic levels, plasmon oscillations, or interband transitions. Trace A of Fig. 20 is the electron loss spectrum obtained from clean CoO where loss peaks are found 8, 15, 34, and 61 eV below the elastic peak. The losses were recorded between 100 and 600 eV incident energy and were invariant at the (100), (111), and center portions of the sample.

When the CoO sample was exposed to the gases listed in Table I, no adsorption effects were observed for the conditions stated. The LEED patterns were unchanged from that of the original surface condition. AES was employed in an attempt to detect C from hydrocarbon or alcohol adsorption and to detect N for nitric oxide or ammonia adsorption. The sample temperature varied according to the charging problems encountered. In all cases where more than $\sim 10^{-7}$ torr pressure is listed, the gate valve was closed and the diffusion pump used to establish a flow of gas through the reaction chamber.

Water, however, was observed to react with CoO - but only in the presence of the electron beam. Trace B of Fig. 20 shows the changes produced in the energy loss spectrum after exposure of CoO to water vapor in the mid 10^{-8} torr range. If the electron beam was moved to a different location on the sample, the

Fig. 20

Electron energy loss spectra from CoO at a metered incident energy of 198 eV. Trace A taken from clean CoO. Trace B after exposure of CoO to water vapor at 6×10^{-8} torr in the presence of the electron beam.

clean CoO energy loss spectrum was obtained. The growth of the 8 eV loss peak with exposure to water was accompanied by a large increase in LEED background and subsequent loss of diffraction spots. After heating the sample to 800°C the energy loss spectrum returned to that seen prior to exposure to the water vapor. When water vapor and cyclopropane were inlet into the reaction chamber simultaneously at $< 10^{-7}$ torr total pressure, the energy loss spectrum of trace B in Fig. 20 was again recorded. Subsequent AES on this electron beam affected area of the sample indicated the absence of surface carbon and hence, cyclopropane chemisorption.

B. Examination of Cr_2O_3

The catalytic properties of chromia, Cr_2O_3 , have been a subject of interest for decades. This material has most notably been applied commercially to the dehydrogenation of olefins and to dehydrocyclization of heptane to toluene. Chromia in the form of a hy-

drated gel requires pretreatment of elevated temperature for development of its catalytic and adsorptive capacity. Burwell²⁸ has proposed that the loss of water during such heating creates coordinatively unsaturated bonds that are the active sites on the catalyst surface. Annealing the hydrated material at a high enough temperature completely releases the bound water and produces crystalline $\alpha\text{-Cr}_2\text{O}_3$. Thus, the interaction of water vapor with Cr_2O_3 is of primary importance to the present study of the material's catalytic properties.

Alpha-chromia exhibits the corundum structure^{29,30} which can be viewed as a slightly distorted hexagonal close-packing of oxygen atoms with metal

TABLE I
EXPOSURE OF CoO TO VARIOUS GASES

Gas Phase	Pressure (torr)	Surface	Comments
Cyclopropane	10^{-5}	Clean	No adsorption, AES, LEED, minutes of exposure, $T = 200^{\circ}\text{C}$, with H_2O present
	10^{-7}	Clean	No adsorption, electron loss, more than 10 min exposure, $T = 200^{\circ}\text{C}$, with H_2O present
Propene	2×10^{-8}	K, Ca impurity	No adsorption, LEED, AES, 1 hr. exposure, $T \sim 25^{\circ}\text{C}$
Methanol	10^{-6}	Clean	No adsorption, LEED, AES, minutes exposure, $T = 200^{\circ}\text{C}$
	10^{-7}	Clean	No adsorption, electron loss, 10 minutes exposure, $T \sim 25^{\circ}\text{C}$
	5×10^{-6}	K, Ca impurity	No adsorption, LEED, AES, 1.5 - 2 hr. exposure, $T \sim 25^{\circ}\text{C}$
Isopropanol	10^{-5}	Clean	No adsorption, LEED after pressure lowered, $T = 175^{\circ}\text{C}$, AES hours after exposure
Toluene	10^{-6}	Clean	No adsorption, LEED, AES, over an hour exposure before 20 min pump-down to 10^{-8} torr range, $T \sim 25^{\circ}\text{C}$
Nitric oxide	5×10^{-8}	Clean	No adsorption, LEED, AES, electron loss, 40 min exposure for AES, $T = 125^{\circ}\text{C}$
Ammonia	3×10^{-8}	Clean	No adsorption, LEED, AES, 30 min exposure, $T = 150^{\circ}\text{C}$

atoms in two-thirds of the octahedrally coordinated holes between the oxygen atoms. When viewed down this stacking axis, i.e. normal to the (0001) plane, the topmost layers of Cr and O appear as in Fig. 21. The unit cell vectors in this plane are as shown in Fig. 21, where $a_o = 4.954\text{\AA}$. Note that because only two-thirds of the octahedrally coordinated holes between oxygen atoms are filled with Cr atoms, the surface mesh is nonprimitive (two Cr atoms per mesh). When examined via LEED, the (0001) net constructed from this nonprimitive mesh produces a hexagonal spot pattern.

The $\alpha\text{-Cr}_2\text{O}_3$ sample used in this study was a wafer of approximately 0.25 cm^2 on each side. It had been cut from a Cr_2O_3 ingot and oriented to expose the (0001) face to within $\pm 1/2^{\circ}$ as verified via x-ray diffraction. The oriented

Fig. 21

Drawing depicting the Cr and O crystallography in the topmost layers of a $\text{Cr}_2\text{O}_3(0001)$ surface. Dots ($\cdot$) indicate Cr atoms. Large circles indicate O atoms. Nonprimitive unit mesh is shown where $\vec{a}_1$ and $\vec{a}_2$ are the unit mesh vectors.

Fig. 22

Hexagonal spot pattern from $\text{Cr}_2\text{O}_3(0001)$ prior to bakeout and any surface treatment in vacuo. Metered incident energy is 156 eV. (00) spot near drift tube.

face was polished with successively finer grit until a 1- μ diamond paste was reached. Immediately prior to placement in the LEED-Auger chamber, the sample was immersed in fused potassium bisulfate at 350°C for two minutes. After removal from the hot etchant and cooling to room temperature, the remnant salt was rinsed away with tap water followed by ultrasonic washing sequentially in deionized water, trichloroethylene, and acetone. The Cr_2O_3 sample was then mounted on the tantalum holder assembly.

Immediately after introduction into the LEED-Auger chamber, i.e. before bakeout, a remarkably sharp LEED pattern was observed from the $\text{Cr}_2\text{O}_3(0001)$ surface as shown in Fig. 22. Individual diffraction spots were still clearly resolvable at metered incident energies as high as 800 eV. AES measurements showed that K was the only significant surface impurity. The ambient gas in the LEED-Auger chamber during these measurements consisted mostly of water vapor (total pressure $\sim 3 \times 10^{-7}$ torr). As was the case with CoO, LEED pattern instabilities and Auger spectrometer noise resulted from sample charging. No further measurements were possible on this Cr_2O_3 sample before filing the final NRIP report. The direction that such measurements should take are discussed in the concluding section of this report.

C. Examination of UO₂

Interest in the catalytic properties of uranium and its compounds has existed since the early 1900s. The relatively recent availability of depleted uranium has prompted continued catalytic investigation of these materials. Reviews^{31, 32} written covering the pre-1960 period of study indicate that uranium oxides have received the bulk of attention on uranium compounds. More recently uranium has been applied to treatment of exhaust gases from internal combustion engines^{33, 34} and its oxides have been analyzed for dehydrogenation and dehydration of ethanol³⁵ and as promoters for iron catalysts in ammonia synthesis.³⁶ Colmenares of Lawrence Livermore Laboratory has investigated the conversion of cyclohexane to benzene on uranium powders at elevated temperatures and atmospheric pressures.³⁷ He has also compiled a bibliography of articles written on the catalysis of thorium and uranium.³⁸

The fully faceted UO₂ (~111) and (~100) "sample one" were examined for their interaction with cyclopropane and propene. This was done in the modified LEED-Augur system without use of the tantalum holder assembly. The samples were mounted next to each other on a stainless steel holder by means of a Pt mesh. No new LEED features were observed from the various faces after exposure to cyclopropane at $\lesssim 2 \times 10^{-8}$ torr for approximately one hour. LEED was also used to examine these surfaces after several minutes of exposure to 5×10^{-6} torr propene prior to poisoning of the electron gun cathode. Again, no new diffraction effects were seen.

D. Discussion

The most notable result derived from this low-pressure study of CoO, Cr₂O₃, and UO₂ is their failure to adsorb any measurable amount of base pressure or intentionally introduced reaction gas. CoO strongly interacted with water vapor - but only in the presence of an electron beam. UO₂ did not chemisorb cyclopropane or propene, and Cr₂O₃ has no affinity for the hydrocarbons typically found in an unbaked vacuum system.

The limitations imposed on the measurements by sample charging (increased sample temperature) and gun cathode poisoning (pressures $\lesssim 10^{-7}$ torr) severely restrict study of such weakly interacting gas-solid combinations. Strong chemisorption should be detectable with these limitations present even if slow surface build-up results from a small sticking coefficient. Sufficient increase in exposure (pressure x time) should yield a measurable surface concentration of

adsorbed reactant gas that does not significantly decrease until well after the pressure is lowered to a value which allows use of the electron gun. For instance, with an exposure at 10^{-6} torr for 5 minutes (where approximately one monolayer of gas molecules is incident on a surface per second) a sticking coefficient of 1/3000 would still give a tenth of a monolayer. With reference to Table I, strong chemisorption certainly did not occur with toluene where not only the exposure time and pressure were large, but also the sample temperature was not elevated.

Methanol has been observed to chemisorb on alumina³⁹ and magnesia⁴⁰ powder at 10^{-5} torr and room temperature. The adsorbed species did not appreciably desorb during a 30-minute pump-out time following the exposure. It would be of definite interest to examine the adsorption properties of large crystalline forms of these materials. Behavior like that of the CoO sample examined in this study would indicate that "active sites," present only in appreciable numbers on powders, are responsible for the alcohol chemisorption.

Measurements have been made of NO adsorption on polycrystalline Co_3O_4 using x-ray photoelectron spectroscopy.⁴¹ The NO adsorption was accomplished at a sample temperature of -100°C and an exposure of 2×10^{-5} torr for 3 hours. The vacuum chamber was then evacuated to the 10^{-7} torr range before the sample was heated. A weak N signal was detectable at 150°C . No measurements were made for exposures above -100°C . It is possible that room-temperature adsorption might be significantly smaller than that found at room temperature after exposing at -100°C . The high surface density of adsorbed molecules attained at -100°C might produce a collective interaction that yields a surface species with stronger bonding properties than possible when molecules are individually adsorbed at room temperature. This line of reasoning suggests that readily detectable adsorbed species may be found on CoO, Cr_2O_3 , or UO_2 at $\lesssim 10^{-7}$ torr through adsorption at low temperature followed by heating to the temperatures used in this study.

V. FINAL SUMMARY

The work presented in this report represents a significant step towards the completion of the first in situ study of heterogeneous catalysis on solid compounds in a LEED-Auger system. Information on the ordering and faceting properties of a totally new set of UO_2 surfaces, vicinal to the (100) face, has been added to the already extensive knowledge on UO_2 in Group CMB-8. The LEED-Auger data clearly indicate that the $\text{UO}_2(\sim 111)$ vicinal surfaces should be preferred

over UO_2 (~100) vicinal surfaces for study of its catalysis as a function of surface crystallography. The modified LEED-Auger system has demonstrated a capability for handling reactant gases up to 10^{-3} torr pressure and, with the addition of a more nonreactive coating, the tantalum holder assembly should prove to meet all its design expectations.

Although the results obtained on CoO , Cr_2O_3 , and UO_2 as regards their interaction with gases are surprisingly uneventful, there are definite directions that future research should take. First, the study of Cr_2O_3 has just begun and complete examination of its chemisorption properties, similar to that done with CoO , may yield positive results. Because of the great emphasis placed on the interaction of water with Cr_2O_3 during activation of the catalyst,²⁸ very thorough investigation of its reactivity with $\text{Cr}_2\text{O}_3(0001)$ is mandatory. Possibly this surface can be activated to hydrocarbon adsorption by the addition of water under the correct temperature and pressure conditions. Second, modifications should be made in the sample holder assembly to allow liquid nitrogen cooling of the sample. This would allow investigation of low-temperature adsorption as discussed at the conclusion of section IV. For this setup UO_2 , with its high electrical conductivity relative to CoO and Cr_2O_3 , would allow the most latitude for experimental measurements. Third, experimental changes should be made to allow neutralization of surface charging using a second electron gun at an appropriate energy. This would immediately allow stable LEED-Auger measurements at and below room temperature on both CoO and Cr_2O_3 .

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