

- <sup>1</sup> F. S. Mortimer, *Spectrochim. Acta* **9**, 270 [1957].
- <sup>2</sup> F. Marsault-Hérail, *J. Chim. Phys.* **68**, 274 [1971].
- <sup>3</sup> L. S. Maïants, E. M. Popov u. M. I. Kabachnik, *J. Opt. and Spectr.* **7**, 108 [1959].
- <sup>4</sup> V. Hornung, O. Aboul Wafa, A. Leutz u. J. Goubeau, *Z. Anorg. Allg. Chem.* **380**, 137 [1971].
- <sup>5</sup> W. Zeil, J. Haase u. L. Wegmann, *Z. Instrumentenkunde* **74**, 84 [1966].
- <sup>6</sup> H. Oberhammer, *Z. Naturforsch.* **25 a**, 1497 [1970].
- <sup>7</sup> D. E. C. Corbridge, in: *Topics in Phosphorus Chemistry*, Vol. 3, Interscience Publishers, S. 211 f.

## Interactions of CO and O<sub>2</sub> with Ir(110) Surfaces

K. Christmann and G. Ertl

Institut für Physikalische Chemie und Elektrochemie, Technische Universität, Hannover, Germany

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LEED/Auger studies with Ir(110) revealed that the clean surface is reconstructed to a  $1 \times 2$ -structure, whereas the normal  $1 \times 1$ -structure can be stabilized by small amounts of carbon impurities. Carbon monoxide adsorbs with a mean heat of adsorption of 37 kcal/mole and forms a  $2 \times 1$ -structure without affecting the substrate "extra" diffraction spots. Adsorbed oxygen forms  $2 \times 2$ - and  $c2 \times 2$ -structures, whereby the diffraction features of the  $1 \times 2$ -structure disappear indicating that oxygen atoms cause place exchange process of the Ir surface atoms which is not the case with adsorbed CO. Carbon monoxide tends to dissociate at elevated temperatures. The catalytic oxidation of CO proceeds in a manner similar to that found with Pd and Pt surfaces.

### 1. Introduction

The platinum metals are successfully used as catalysts for the oxidation of carbon monoxide and the chemisorption of these gases has been frequently studied. Investigations with clean single crystal surfaces using low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) have been performed particularly with platinum<sup>1, 2</sup> and palladium<sup>3–6</sup>. Grant<sup>7, 8</sup> reported the only (and not very extensive) results for Ir (111) and (100) surfaces. The clean Ir(100) surface exhibits not the normal periodicity of the surface atoms as expected from the termination of the bulk structure, but a reconstructed  $5 \times 1$ -structure, which is (similar as in the case of Au and Pt) attributed to the existence of a hexagonal structure of the topmost atomic layer<sup>7, 9</sup>. In the following some investigations with a Ir(110) surface using LEED and AES will be described. This surface has also been found to deviate from the ideal lattice periodicity which causes some interesting consequences for the adsorption properties.

### 2. Experimental

The investigations were performed with a commercial LEED/Auger system (Varian) using a 4

grid optics and an additional glancing angle electron gun for Auger spectroscopy. A quadrupole mass spectrometer (Finnigan) served for recording flash desorption spectra and for monitoring the residual gas composition.

The sample was prepared as a cylindrical slice (diameter 6 mm, thickness 1 mm) from an Ir single crystal (purity 99.999%; Metals Research) by means of spark erosion. The sample holder consisted of two spot welded Ta wires which also served for resistance heating of the crystal. Temperature measurements were achieved by a small Pt/PtRh thermocouple spot welded to the sample. The base pressure of the vacuum system was in the low  $10^{-10}$  Torr range.

The sample surface was first mechanically polished (minimum grain size  $0.25 \mu$ ) and subsequently treated by different etching and electropolishing procedures. The best results were achieved with a melt of  $\text{NaNO}_2$ , which however caused the formation of a thick oxide layer on the surface. Cleaning the surface in vacuo was a difficult task. The complete treatment included the following steps: a) oxygen treatment at  $1000^\circ\text{C}$  and subsequent annealing at  $1200^\circ\text{C}$  for a long period of time; b) argon ion bombardment (energy 450 eV, current density  $\sim 10^{-6} \text{ A/cm}^2$ ) for 500 h; c) annealing at  $700^\circ\text{C}$ . The most pertinent surface contaminant was carbon which was identified by AES and diffuses into the bulk at elevated temperatures. Figure 1 shows an Auger spectrum of a clean and of a partially contaminated surface. No traces of impurities were detected in the former case.

Reprint requests to Prof. Dr. G. Ertl, Physikalisch-Chemisches Institut der Universität, D-8000 München, Sophienstraße 11 (present address).



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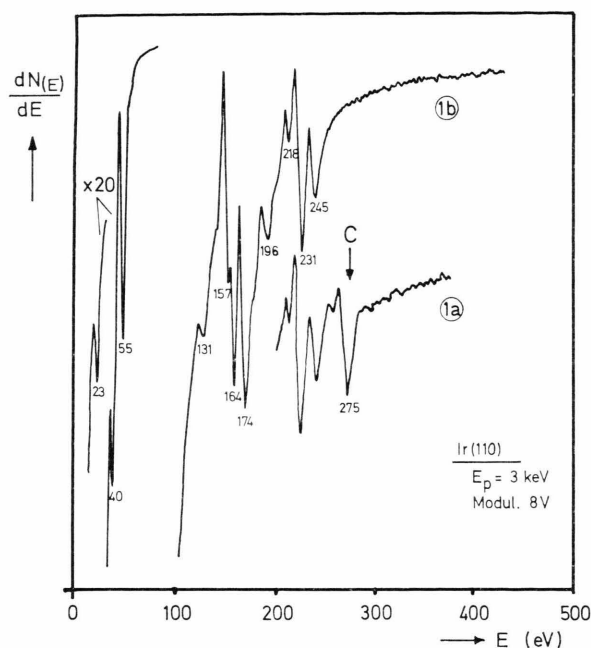


Fig. 1. Auger electron spectra from Ir(110) surfaces.  
a) with carbon contamination, b) clean surface.

### 3. Results

#### 3.1. The Ir(110) surface

Carbon contamination of the surface may give rise to the formation of  $c2 \times 2$ -structure whose LEED pattern is shown in Figure 2\*. Subsequent argon ion bombardment at room temperature leads to the appearance of a  $1 \times 1$ -structure, that means the surface exhibits the same periodicity as the bulk (Figure 3 a). However, the surface with  $1 \times 1$ -structures were never completely free of trace amounts of C, which may for example be formed by decomposition of CO which is contained in the residual gas during the ion bombardment. It cannot be excluded that small amounts of carbon are stabilizing the  $1 \times 1$  surface structure. This structure is thermally unstable. Upon heating the crystal at about 300 °C to 400 °C streaks in [01]-directions of the LEED pattern are formed (Fig. 3 b) which finally coalesce into additional spots of a  $1 \times 2$ -structure (Figure 3 c). The carbon diffuses from the surface into the bulk during the treatment as demonstrated by AES; the  $1 \times 2$ -structure represents the stable stage of the clean Ir(110) surface without any detectable impu-

rities. Mostly the additional diffraction spots were not as sharp as in Fig. 3 c but somewhat elongated in the [01]-direction indicating a certain degree of anisotropic disorder within the surface periodicity.

#### 3.2. Adsorption of carbon monoxide

When CO was admitted at room temperature to a (metastable) surface with  $1 \times 1$ -structure streaks in the LEED pattern in [10]-direction between the substrate spots appeared after an exposure of about 0.3 L ( $1 L = 10^{-6}$  Torr·sec) which with increasing exposure developed into spots of a  $2 \times 1$ -structure (Figure 4 a). It has to be noticed that the "extra" spots ( $\frac{1}{2}, 0$ ) and  $(-\frac{1}{2}, 0)$  were missing.

The same experiment was performed with a clean surface with  $1 \times 2$ -structure and again a  $2 \times 1$ -structure was formed, however, without affecting the original spots due to the  $1 \times 2$ -structure (Figure 4 b).

Heating the sample above 200 °C in a CO atmosphere leads to an irreversible transformation from the  $2 \times 1$ - into a  $c2 \times 2$ -structure. This result is interpreted as due to the dissociation of CO which is supported by further observations. Figure 4 c shows a somewhat diffuse diffraction pattern consisting of a superposition of the diffraction spots of  $2 \times 1$  ( $CO_{ad}$ ) and  $c2 \times 2$  ( $C_{ad} + O_{ad}$ ) structures, which form different domains on the surface. Heating in vacuo made first disappear the  $2 \times 1$ -structure and at higher temperatures also the  $c2 \times 2$ -structure.

The region of stability of the ordered CO structure was determined as a function of CO pressure and temperature. The points in Fig. 5 are marking the stages at which the  $2 \times 1$ - "extra" spots just became visible, they all therefore represent a definite degree of coverage. From this plot the isosteric heat of adsorption at this particular coverage may be derived using the Clausius-Clapeyron equation<sup>4</sup>. A value of 37 kcal/mole results in our case. With these measurements care had to be taken that the reversible adsorption-desorption equilibrium was not disturbed by the decomposition reaction of CO.

Finally some flash desorption spectra were taken by rising the temperature of the CO covered surface monotonically (5 °C/sec) and recording the CO partial pressure as a function of time. Starting with a  $2 \times 1$ -CO structure a single desorption peak at about 175 °C was detected (Fig. 6, curve a). When the diffraction pattern consisted of superimposed spots from  $2 \times 1$ - and  $c2 \times 2$ -structures a more complicated spectrum was obtained (curve 6 in Fig. 6). In

\* Fig. 2, 3, 4 and 7 on page 1148 a, b.

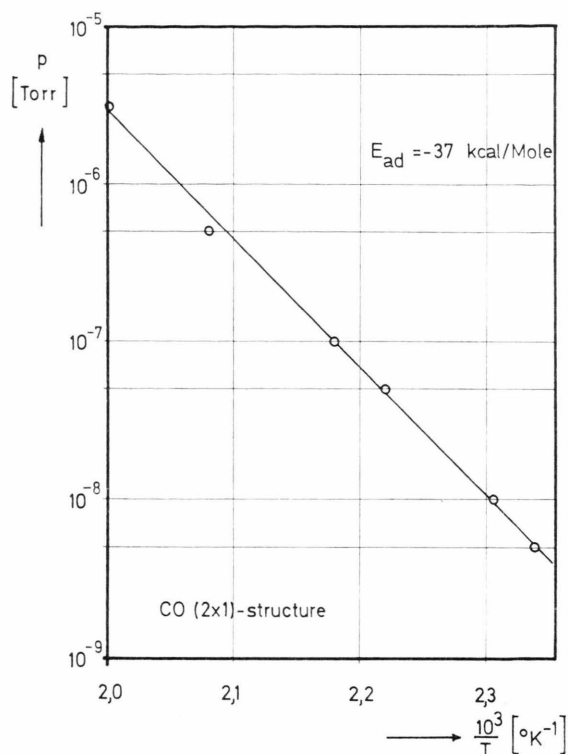
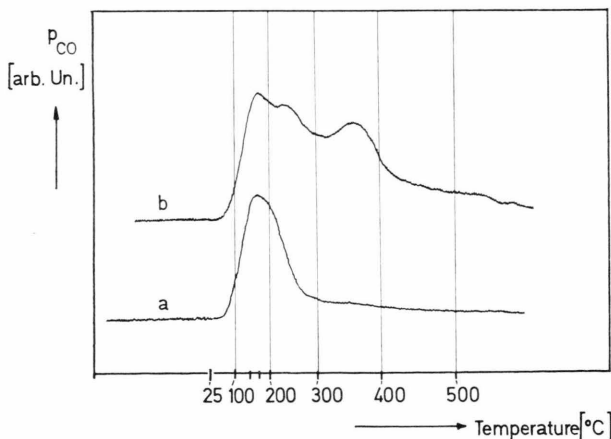
Fig. 5. Diagram of stability of the  $2 \times 1$ -CO-structure.

Fig. 6. Flash desorption spectra from CO covered Ir(110) surfaces. a) Without decomposition of adsorbed CO, b) with partial dissociation of adsorbed CO.

addition to the maximum at 175 °C two peaks at higher temperatures were observed, similar to the results with CO covered Ni(110) <sup>10</sup>.

### 3.3. Adsorption of oxygen

Only a stable and clean surface with a somewhat imperfect  $1 \times 2$ -structure (i. e. with a streaked "ex-

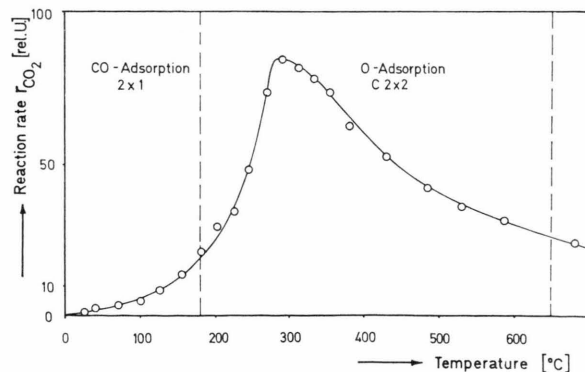
tra" spots) was used for the study of oxygen adsorption. An oxygen exposure of 0.5 L at room temperature causes the appearance of a  $2 \times 2$ -diffraction pattern which replaces the diffraction features of the clean  $1 \times 2$ -surface. Mild annealing at about 100 °C leads to sharpening of the additional new spots due to surface diffusion and more perfect order in the adsorbed layer (Fig. 7 a). This observation clearly indicates, that adsorbed oxygen is able to destroy the superstructure (with imperfect periodicity) of the clean surface.

This effect becomes even more pronounced if the crystal is exposed to oxygen at 400 °C. The  $1 \times 2$ -spots disappeared completely (Fig. 7 b), and upon cooling the sample in an oxygen atmosphere sharp additional spots of a  $c2 \times 2$  structure became visible (Figure 7 c).

In both adsorbate structures oxygen is tightly bound to the surface and may only be removed by flashing the sample to about 600 °C. The clean surface subsequently exhibited again the pattern of a  $1 \times 2$ -structure with elongated "extra" spots.

### 3.4. Catalytic oxidation of carbon monoxide

The stationary rate of CO<sub>2</sub> formation in a CO/O<sub>2</sub> mixture (1 : 1) with a total pressure of  $2 \cdot 10^{-7}$  Torr was measured as a function of surface temperature using the quadrupole mass filter. With a steady state flow system the reaction rate is directly proportional to the partial pressure of the formed product. The result is shown in Figure 8. At room temperature the rate of CO<sub>2</sub> formation is negligibly small and increases only at about 100 °C parallel to the onset of CO desorption as realized by simultaneous observation of the diffraction pattern. A maximum is

Fig. 8. Steady-state rate of CO<sub>2</sub> formation in a CO/O<sub>3</sub> mixture as a function of temperature.

reached around 300 °C where the oxygen coverage also reaches maximum values. At still higher temperatures the stationary oxygen coverage decreases due to beginning desorption competing with the catalytic reaction and consequently also the rate of reaction decreases. These observations are in complete agreement with those made with Pd(110) <sup>4</sup>.

#### 4. Discussion

Some of the surfaces of the elements Ir, Pt and Au are unique among metal surfaces in so far as they have structures which differ from those to be expected from a simple termination of the bulk lattice. These effects have been investigated in detail with their (100)-surfaces, where the observed LEED patterns are ascribed to the existence of hexagonal surface layers. The Ir(100) surface was studied extensively by Ignatiev et al. <sup>9</sup>. If it is free from impurities this surface exhibits a  $5 \times 1$ -superstructure, whereas small amounts of carbon may stabilize the normal  $1 \times 1$ -structure. The authors could demonstrate convincingly that the  $5 \times 1$ -structure is caused by a somewhat distorted hexagonal overlayer, that means the structure is compressed in the [221] direction by about 4% as compared with the normal (111) plane.

Rhodin et al. <sup>13</sup> discussed some of the reasons which account for hexagonal surface layers on the 5d-metals Ir, Pt and Au with an increased number of nearest neighbours being energetically more favourable. This tendency should also be existent with the (110)-surfaces of these metals, whereas the (111)-surfaces should exhibit their normal structures. The latter fact has indeed be demonstrated for Ir(111) <sup>8</sup> and Pt(111) <sup>1</sup>.

Altered periodicities have been observed with the (110) surfaces as expected. Fedak and Gjostein <sup>14</sup> reported for Au(110) a  $1 \times 2$ -structure, which transforms reversibly into a  $1 \times 1$ -structure above 600 °C. Bonzel and Ku <sup>2</sup> observed also a  $1 \times 2$ -structure with Pt(110), whereas Berthier et al. <sup>15</sup> reported the formation of  $1 \times 2$ - and  $1 \times 3$ -structures in this case. The results of the present work, whereafter a clean Ir(110) surface exhibits a  $1 \times 2$ -structure agree completely with the general picture. A further analogy is remarkable: As in the case of Ir(100) the normal  $1 \times 1$ -structure of Ir(110) may be stabilized by small amounts of carbon impurities.

In contrast to the  $5 \times 1$ -structures of clean (100) surfaces it is not possible to interpret the reconstructed  $1 \times 2$ -structure of Ir(110) with the existence of a hexagonal overlayer if realistic diameters of the Ir atoms are taken into consideration. In order to derive plausible models more detailed investigations are necessary. Probably the  $1 \times 2$ -structure is caused by a pairwise mutual approach of the top-most atomic layers. The stable  $1 \times 2$ -structure is frequently not characterized by a perfect two-dimensional order but may deviate in the [01]-direction from the double-spaced periodicity as indicated by the streaks in the diffraction pattern.

It is interesting to regard the behaviour of the surface periodicity under the influence of adsorbed particles: Adsorption of CO does not influence the "extra" spots of the clean surface structure, but these disappear in presence of adsorbed oxygen. (With the  $0.2 \times 2$ -structure the sharp halforder spots are by no means identical with the streaky additional spots of the  $1 \times 2$ -structure.) The conclusion is that Ir surface atoms are moving under the influence of adsorbed oxygen. The possibility of "reconstructive" or "corrosive" adsorption had been proposed already some years ago based on LEED <sup>16</sup> and field ion microscopic studies <sup>17</sup> and was also the subject of extensive discussion. The here observed disappearance upon adsorption of LEED spots originating from reconstructed substrate surfaces is obviously an unique means to demonstrate the occurrence of such effects.

The adsorption of oxygen on Ir(100) does not cause the disappearance of the  $5 \times 1$ -diffraction pattern <sup>7</sup>. This result seems to be plausible if the hexagonal surface layer which is responsible for this pattern is considered. On the other hand displacements of surface atoms under the action of adsorbed atoms appear to be easier possible with the open Ir(110) surface.

The interaction between CO and Ir(110) is much weaker and therefore no displacement of surface atoms occurs. It is remarkable that  $2 \times 1$ -CO-structures are formed on the  $1 \times 1$  as well as on the  $1 \times 2$ -surfaces, which may probably be considered as a hint that the atomic displacements of the Ir(110)- $1 \times 2$ -surface are not connected with a radical variation of the atomic arrangements [as is the case for example with Ir(100)].

Adsorption of CO leads also at Pd(110) <sup>4,6</sup> and Ni(110) surfaces <sup>18</sup> to the formation of a  $2 \times 1$ -

structure with missing or only weak ( $\frac{1}{2}$ , 0) and ( $-\frac{1}{2}$ , 0) spots. A model for this structure has been published<sup>18</sup> which seems to be highly probable and should also be applicable for the CO/Ir(110) system. Thereafter the adsorbed CO molecules form a densely packed structure with a coverage  $\Theta = 1$ . The value of 37 kcal/mole for the mean heat of adsorption as derived in this work is also in good agreement with data for Pd(110)<sup>4, 6</sup>.

At higher sample temperatures CO may dissociate at Ir(110) indicated by the formation of a  $c2 \times 2$ -LEED pattern as also found with adsorbed carbon and oxygen layers. This leads to the occurrence of additional maxima at higher temperatures in the flash desorption spectra due to the increased activation energy for desorption via surface recombination. Analogous observations were made with a Ni(110) surface, where the mechanism of the CO decomposition has been discussed in more detail<sup>10</sup>. On the other hand with Pd(110) no dissociation of

CO and only a single desorption peak was observed.

Desorption of oxygen from Ir(110) occurs in a temperature range similar to that found with Pd(110), but the present data are too scant for a quantitative comparison. With Ni(110) no oxygen desorption but incorporation into the bulk takes place<sup>19</sup>.

The steady-state formation of CO<sub>2</sub> from a CO/O<sub>2</sub> mixture as a function of temperature proceeds quite similar on Ir(110) as on Pd(110)<sup>4, 5</sup> and on Pt(110)<sup>2</sup>. The same mechanism as derived for the reaction at palladium is therefore also assumed for the iridium catalyzed reaction. This takes place predominantly between adsorbed oxygen atoms and gaseous CO (Eley-Rideal mechanism), whereby adsorbed carbon monoxide inhibits the adsorption of oxygen. At lower temperature the desorption of CO is rate determining; at high temperatures the rate of CO<sub>2</sub> formation decreases again owing to the desorption of oxygen.

- <sup>1</sup> a) C. W. Tucker, *J. Appl. Phys.* **35**, 1897 [1964]. b) A. E. Morgan and G. A. Somorjai, *J. Chem. Phys.* **51**, 3309 [1969]; *Surface Sci.* **12**, 405 [1968]. c) W. H. Weinberg, R. M. Lambert, C. M. Comrie, and J. W. Linnett, *Proc. 5-th Int. Congress on Catalysis*, Palm Beach 1972; North Holland, Amsterdam 1973, in press. d) B. Lang, R. W. Joyner, and G. A. Somorjai, *Surface Sci.* **30**, 454 [1972].
- <sup>2</sup> H. P. Bonzel and R. Ku, *J. Vac. Sci. Techn.* **9**, 663 [1972].
- <sup>3</sup> a) R. L. Park and H. H. Madden, *Surface Sci.* **11**, 188 [1968]. b) J. C. Tracy and P. W. Palmberg, *J. Chem. Phys.* **51**, 4852 [1969]. c) G. Ertl and J. Koch, *Z. Phys. Chem. N.F. (Frankfurt)* **69**, 323 [1970]; *Z. Naturforsch.* **25a**, 1906 [1970]; in: *Adsorption-Desorption Phenomena*, F. Ricca, ed., Academic Press 1972, p. 345.
- <sup>4</sup> G. Ertl and P. Rau, *Surface Sci.* **15**, 443 [1969].
- <sup>5</sup> G. Ertl and J. Koch, *Proc. 5-th Int. Congress on Catalysis*, Palm Beach 1972, North Holland, Amsterdam 1973 (in press).
- <sup>6</sup> H. Conrad, G. Ertl, J. Koch, and E. E. Latta, in preparation.
- <sup>7</sup> J. T. Grant, *Surface Sci.* **18**, 228 [1969].
- <sup>8</sup> J. T. Grant, *Surface Sci.* **25**, 451 [1971].
- <sup>9</sup> A. Ignatiev, A. V. Jones, and T. N. Rhodin, *Surface Sci.* **30**, 573 [1972].
- <sup>10</sup> H. H. Madden and G. Ertl, *Surface Sci.* **35**, 211 [1973].
- <sup>11</sup> S. Hagstrum, H. B. Lyon, and G. A. Somorjai, *Phys. Rev. Lett.* **15**, 491 (Pt) [1969].
- <sup>12</sup> a) P. W. Palmberg and T. N. Rhodin, *Phys. Rev.* **161**, 586 [1967]. b) D. G. Fedak and N. A. Gjostein, *Surface Sci.* **8**, 77 (Au) [1967].
- <sup>13</sup> T. N. Rhodin, P. W. Palmberg, and E. W. Plummer, in: *The structure and chemistry of solid surfaces* (G. A. Somorjai, ed.), Wiley, New York 1969, p. 22-1.
- <sup>14</sup> D. G. Fedak and G. A. Gjostein, *Acta Met.* **15**, 827 [1967].
- <sup>15</sup> Y. Berthier, M. Perdureau, and J. Oudar, *Surface Sci.* **36**, 225 [1973].
- <sup>16</sup> See for example: J. W. May, *Adv. Catalysis* **21**, 151 [1970].
- <sup>17</sup> A. A. Holscher and W. M. H. Sachtler, *Disc. Faraday Soc.* **41**, 29 [1966].
- <sup>18</sup> a) T. N. Taylor and P. J. Estrup, *J. Vac. Sci. Techn.* **10**, 26 [1973]. b) H. H. Madden, J. Küppers, and G. Ertl, *J. Chem. Phys.* **57**, 3401 [1973].
- <sup>19</sup> J. W. May and L. H. Germer, in: *The Structure and Chemistry of Solid Surfaces*, G. A. Somorjai, ed., John Wiley, New York 1969, p. 51-1.



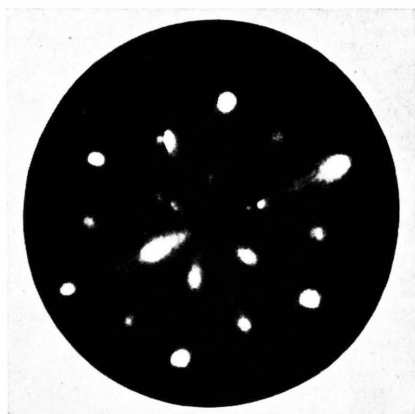


Fig. 2. LEED pattern of a  $c2 \times 2$ -C-structure.

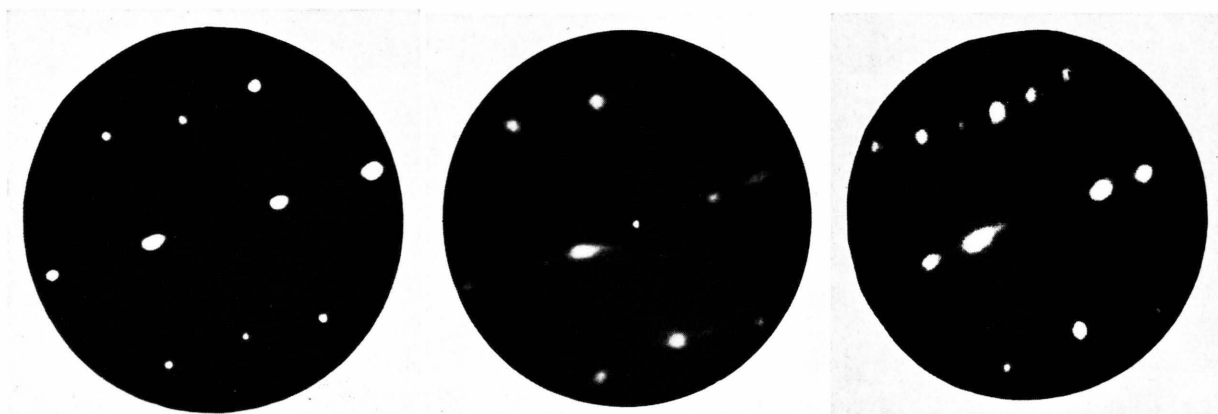


Fig. 3. LEED patterns of Ir(110) surfaces. a)  $1 \times 1$ -structure, b) diffraction pattern with streaks (transformation  $1 \times 1 \rightarrow 1 \times 2$ ), c)  $1 \times 2$ -structure.

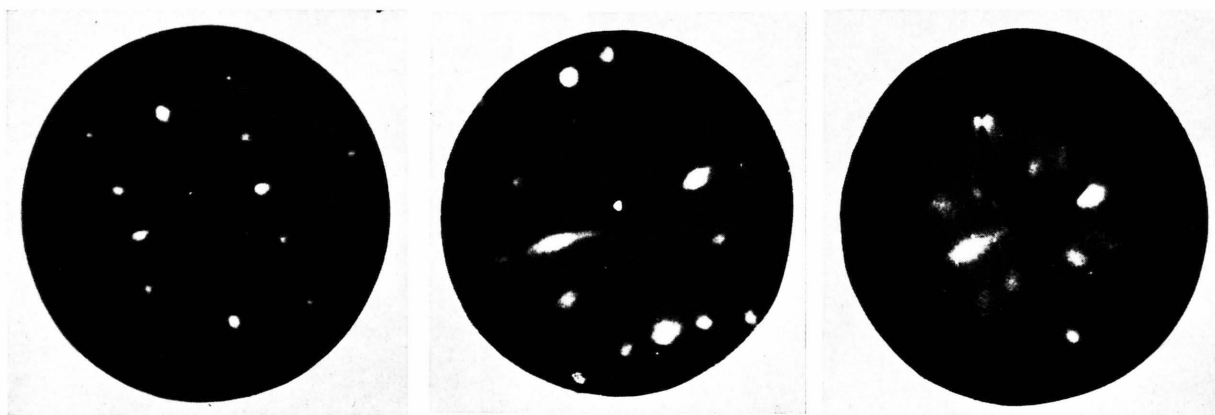


Fig. 4. LEED patterns of CO covered Ir(110) surfaces. a)  $2 \times 1$ -structure after saturation of the adsorbate layer (Ir surface with  $1 \times 1$ -structure), b)  $2 \times 1$ -structure (Ir surface with  $1 \times 2$ -structure), c)  $2 \times 1$ - and  $c2 \times 2$ -structure at initial decomposition of adsorbed CO.

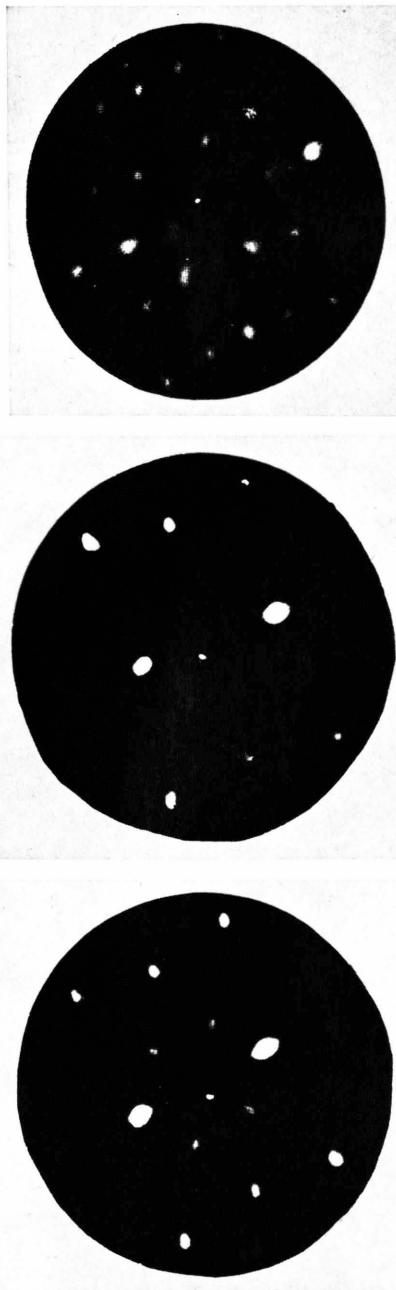


Fig. 7. LEED patterns of oxygen covered Ir(110) surfaces. a)  $2 \times 2$ -structure, b)  $1 \times 1$ -structure after interaction with  $O_2$  at  $400^\circ C$ , c)  $c2 \times 2$ -structure after cooling in  $O_2$  atmosphere.