

First Steps in the Oxidation of a (110) Nickel Surface

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ABSTRACT

Oxygen is initially adsorbed upon a (110) nickel surface with unit sticking probability. At  $1/3$  coverage there are two different phases. At room temperature there is a well ordered (3 x 1) structure, which agglomerates at  $300^{\circ}\text{C}$  into a poorly organized (2 x 1) structure. Between  $1/2$  and  $2/3$  coverage at  $300^{\circ}\text{C}$  there is a set of superstructures of gradually increasing oxygen content, made up of (2 x 1) and (3 x 1) units uniformly distributed within repeating sequences. This behavior is quite different from the disorder found in this range when adsorption takes place at room temperature. When oxygen is removed from the surface by hydrogen at  $300^{\circ}\text{C}$ , sharp superstructure spots are seen in the reverse order until the surface is clean.

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Adsorption of oxygen upon a clean metal surface and the beginning of oxidation are so closely related that their separation becomes a matter of definition, and experiments upon nickel surfaces have led to the conclusion that oxidation of these surfaces occurs at once with the very first exposure to oxygen.

In LEED studies of the adsorption of oxygen at room temperature upon a (110) face of a nickel crystal it has been reported that several successive surface structures are formed before the coverage is as great as two-thirds of a monolayer<sup>1-5</sup>; these have progressively larger numbers of oxygen atoms per unit area. The LEED experiments to be described here have extended this work to discover some

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details previously overlooked. They show also that for adsorption at 300°C complex superstructures are produced while the coverage is being increased from one-half to two-thirds of a monolayer. These superstructures have a certain disorder if the temperature is never raised above 30°C, and were not clearly recognized earlier.

Experimental procedures have been described elsewhere<sup>3</sup>. The (110) nickel surface was cleaned by argon bombardment followed by vacuum anneal at 1000°K for a time that was kept very short to minimize contamination by residual gas. Oxygen was admitted through a bakeable leak valve. Contamination by CO was very low<sup>6</sup>. Oxygen pressures were measured with a mass spectrometer and checked against an ion gauge.

In a typical experiment oxygen pressure was raised abruptly from substantially zero to a predetermined level, held there for an appropriate interval, then rapidly dropped to a negligible value by closing the valve. This exposure produces in general a significant modification of the initial diffraction pattern from that of the clean surface. The pattern can be changed progressively in steps by such repeated exposures. Control tests showed that any particular diffraction pattern obtained after a series of exposures of this sort is stable for at least as long a time as was needed to finish a series of experiments. Exposures to produce particular changes agree with those published earlier<sup>1-3</sup>.

## COVERAGE OF LESS THAN ONE-HALF MONOLAYER

In Figure 1 are shown diffraction patterns from a clean surface, from the same surface after an oxygen exposure of  $0.4 \times 10^{-6}$  torr-sec (which we call 0.4L, using L as an abbreviation for Langmuir)<sup>7</sup>, and after an exposure of 0.8L. The oxygen coverage for Figures 1B and 1C was about 1/3 monolayer, and the pattern obtained at room temperature (B) is that of a (3 x 1) structure. Raising the temperature of this surface to 300°C resulted in the pattern of Figure 1C which is obviously caused by a somewhat disorganized (2 x 1) structure<sup>8</sup>. With this oxygen coverage close to 1/3 the pattern can be changed back and forth quite reversibly from (2 x 1) at 300°C to (3 x 1) at 30°C. In other tests it was found that the pattern for this coverage is predominantly (2 x 1) rather than (3 x 1) down to temperatures at least as low as 200°C. At 300°C the slightly diffuse (2 x 1) structure was stable for a considerable time, indicating no significant contamination from residual gas and no appreciable influence of oxygen diffusion into the crystal interior during the time of an experiment. The reversible alteration between (2 x 1) and (3 x 1) upon heating and cooling shows that we were dealing with an unchanging amount of oxygen in a closed system. This opens a way to future theoretical analysis.

We conclude that one-third of a monolayer of oxygen can exist on the surface in one or the other of two different phases. At 30°C the stable arrangement is apparently a uniform (3 x 1) structure over the entire surface. At 300°C essentially all the surface O is in the stable arrangement of clusters of the half-monolayer (2 x 1) structure, and we presume that these clusters cover two-thirds of the surface leaving one-third effectively bare. The (2 x 1) pattern is more diffuse than the (3 x 1) pattern and we can attribute this to the limited sizes of the (2 x 1) islands or to a certain disorder in the [110] surface direction.

Although we do not know why the (3 x 1) structure of Figure 1B was never found before, we can speculate that in some of the earlier work the crystal may have been still too warm from previous annealing when exposed to oxygen for the first time, and the coverage may have become greater than 0.3 before cooling.

The (3 x 1) structure giving the pattern of Figure 1B is made of units 3 spacings long in the close packed [110] surface direction. Each unit contains a single O atom. Because the coverage is 1/3 of a monolayer we call this the O[1/3] structure. We can imagine it as the atomic sequence -Ni-O-Ni- repeating over and over in the [110] direction with all such parallel chains "in step." This model of a reconstructed surface is based on previous conclusions concerning oxygen adsorption on nickel

surfaces<sup>1-5</sup>. The reconstruction hypothesis has, however, recently been questioned<sup>9-11</sup>, so that we should also consider the  $O[1/3]$  structure in terms of triple spaced  $O$  atoms lying on top of an undisturbed nickel substrate.

We need not, however, choose between these special models to explain our results. The  $O[1/3]$  structure, and also structures we observe at higher coverage, can be thought of in terms of repeat units for which only the length and oxygen content need be specified, and our results can be entirely explained in terms of these more general units.

#### COVERAGE BETWEEN ONE-HALF AND TWO-THIRDS MONOLAYER

When oxygen exposure of a  $[110]$  nickel surface is continued at room temperature to  $0.8L$ , the pattern of Figure 1B changes into the fully developed  $(2 \times 1)$  pattern of  $1/2$  a monolayer of  $O$  atoms, the  $O[1/2]$  structure. With further exposure the now sharp  $h+\frac{1}{2}, k$  diffraction spots become streaked parallel to the  $[110]$  direction lying in the surface plane<sup>1-3</sup>. With continuing exposure these streaks gradually resolve themselves at about  $5L$  into sharp spots which are at the  $h+\frac{1}{3}, k$  positions shown in Figure 2. We have good reasons to believe that this second  $(3 \times 1)$  pattern represents two-thirds of a monolayer of oxygen atoms<sup>12</sup>, which we call the  $O[2/3]$  structure.

The  $O[1/2]$  structure is made of units two spacings long in the  $[110]$  surface direction, each unit containing a single oxygen atom. The  $O[2/3]$  units, on the other hand, are three spacings long in the  $[110]$  surface direction and contain just two oxygen atoms.

The new observations, which we report here, are concerned with superstructures that can be produced in coverages intermediate between one-half and two-thirds of a monolayer. The streaks appearing when exposure is carried out at room temperature are evidence of disorder along the  $[110]$  surface direction, presumably with a mixture of the  $O[1/2]$  and  $O[2/3]$  sequences. After anneal at very moderate temperatures the randomness in the arrangement of these sequences is replaced by superstructures.

The experiment was carried out with exposure to oxygen while the crystal was held at  $300^{\circ}\text{C}$ . The streaks appearing after room temperature exposure are not present. In their place are sharp spots having separations which appear to vary continuously with exposure and are appropriate to a sequence of superstructures.

In experiments leading to Figures 3, 4 and 5 the clean surface was exposed to oxygen at  $2 \times 10^{-8}$  torr for various lengths of time while the crystal was held at  $300^{\circ}\text{C}$ . Many of the exposures were fifteen seconds long giving increments



of exposure of 0.3L. Between successive oxygen exposures the crystal heating current was turned off for several seconds just long enough to photograph the diffraction pattern. In all cases the total oxygen exposures lay in the range between 0.8 and 5L, giving coverages of more than one-half monolayer.

One of these photographs is reproduced as Figure 3. This was taken after an oxygen exposure of 1.8L. On this photograph the  $h+1/2$  diffraction spots characteristic of half a monolayer are split into two spots having a separation measured to be the fraction  $F = 0.17$  of the spacing between the  $0 \bar{1}$  and  $1 \bar{1}$  spots.

Measurements of the fraction  $F$  on different photographs have shown the variation with exposure represented in Figure 4. A linear relation between  $F$  and oxygen exposure implies, if the sticking probability is uniform in this range and if the oxygen is really contained in the top layer as we assume, that the coverage of oxygen expressed as a fraction of a monolayer  $\theta$  is given by  $\theta = 0.5 + F/2$ . The ordinates of Figure 4 then represent coverage  $\theta$  as well as values of  $F$ ,  $\theta$  varying linearly from 0.5 at  $F = 0$  to 0.67 at  $F = 0.33$ . Then the slope of the graph gives a value of sticking probability at 300°C of 0.12 in this range of coverages.

The same data are shown more strikingly in Figure 5. Here are reproduced strips taken from many of the photographs

upon which Figure 4 is based, such as Figure 3. The horizontal spacings of these strips are arranged to represent oxygen exposure. Straight lines drawn between the photographs illustrate the linear increase of the splitting with exposure<sup>13</sup>.

We have checked that diffusion of oxygen into the interior of the crystal does not materially affect our results. Figure 6A shows a pattern obtained after an oxygen exposure of 2.4L at 300°C. Figures 6B and 6C were then obtained by heating the crystal at 300°C for 30 seconds and 150 seconds with the oxygen valve shut and the pressure substantially zero. At an experimental oxygen pressure of  $2 \times 10^{-8}$  torr the splitting increases by about 1 percent per second (Figure 4), but the patterns of Figure 6 show no measurable decrease in splitting due to oxygen diffusion into the interior.

#### INTERPRETATION

The apparently continuous variation of the splitting fraction  $F$  with oxygen exposure seems at first difficult to understand. For example, a value of  $F$  expressed as the quotient of two rather large numbers seems to imply a superstructure with an absurdly long domain size. That this is really not required has, however, been pointed out by Fujiwara<sup>14</sup>. He has considered superstructures in which the arrangement is not uniform but the mixing is approximately

uniform. In our case this means that the oxygen coverage is closely uniform over any area not unreasonably small. For such deviations from perfect superstructure Fujiwara shows that the positions of superstructure lines and also their intensities will be altered only very little from the values they would have for a perfect arrangement.

We now adopt a convenient shorthand. To the unit of the  $O[1/3]$  structure, symbolized by  $-Ni-O-Ni-$ , we assign the letter A, so that the  $O[1/3]$  structure is written  $-A-A-A-$ . Similarly, to the  $O[1/2]$  and  $O[2/3]$  units symbolized by  $-O-Ni-$  and  $-O-Ni-O-$ , we assign the letters B and C, writing for  $O[1/2]$  and  $O[2/3]$  respectively  $-B-B-B-$  and  $-C-C-C-$ . The sole restrictions on the symbolic units A, B or C are that they are 3, 2 or 3 spacings long in the  $[110]$  surface direction and respectively contain 1, 1 or 2 oxygen atoms.

We propose that the sharp superstructure spots in the photographs of Figure 5, and in others not reproduced here, result from uniform mixtures of the two sequences B and C. Then, if the relative numbers of these two sequences are respectively  $N_B$  and  $N_C$ , the ratio of these numbers  $R = N_C/N_B$  is simply related to the fraction F by  $R = 2F/(1-3F)$  - ranging from  $R = 0$  at  $F = 0$  to  $R = \infty$  at  $F = 1/3$ . If the two possible sequences were arranged as symmetrically as possible along every  $[110]$  line of surface atoms, and if adjacent lines were "in step" they would give

rise to sharp superstructure diffraction spots. Simple calculations indicate that the strongest of these are a pair of variable separation just as we actually find. Other much weaker spots are predicted also, with these weaker spots strongest for values of  $F$  for which  $N_B$  and  $N_C$  are approximately equal.

On Figure 5 several of these weaker superstructure spots are clearly visible. They are most plain for  $F = 0.2$  and are at just the correct positions dividing the spacing between the normal nickel spots into fifths (in the figure this is the fifth strip from the left). The ideal superstructure for  $F = 0.2$  has a unit mesh containing just one of each of the sequences B and C (i.e.  $R = 1$ ), and is written  $-BC-BC-BC-$ . This is probably the same  $(5 \times 1)$  structure of coverage  $3/5$  reported previously by Germer and MacRae<sup>1-3</sup>, and is an equally weighted mixture of the  $O[1/2]$  and  $O[2/3]$  sequences.

Now  $3/5$  of a monolayer of O can be arranged in only two fundamentally different  $(5 \times 1)$  units, symbolized by  $-ONiONiO-$  which is just  $-BC-$ , and by  $-NiOOONi-$  which is the less uniform arrangement and which violates our proposed short range order. Because at room temperature the only well-ordered structures are  $(2 \times 1)$  and  $(3 \times 1)$ , we infer that the second of these arrangements is improbable because it contains subunits other

than B and C. Calculations support this idea. Intensities are calculated for ideal meshes of one-dimensional symmetry considering scattering from one kind of atom only (top layer nickel atoms if we have a reconstructed surface). Phases are simply added in the standard kinematical treatment. Relative intensity distributions shown in Figure 7 and calculated in this primitive fashion should be taken as qualitatively illustrating general features of our model. The distribution for  $-ONiONiO-$  compares favorably with Figure 5, but that for  $-NiOONi-$  does not. We have repeated this calculation systematically in our coverage range for cells up to ten units long, with the result that the appropriate superstructure spots, and not others, are only strong when the cell is constructed of B and C building blocks. The cell is then most uniform for all these cases.

For cells up to this size only one coverage and only one arrangement of these blocks is possible. Larger cells can be generally satisfied by different proportions of B and C so that different coverages for a given length can occur. An additional feature for large cells of given length and coverage (taken to be ideal in this discussion) is that they can have their component blocks arranged with differing degrees of uniformity. Our calculations indicate that the favored arrangement has the most uniform long range order within the cell.

As an example we consider a cell seventeen spacings long. This is the smallest cell where there are three possible values of  $\theta$ , and we deal first with cells having the most uniform distribution of B and C. For  $\theta = 9/17$  we have -BBBBBBBC- which differs only slightly from a proper  $O[1/2]$  sequence. For  $\theta = 10/17$  the most uniform repeating sequence -BCBCBCB- is only a little different from the  $O[3/5]$  structure, and for  $\theta = 11/17$  we have -BCCCCC- which is close to being  $O[2/3]$ . One expects these three sequences to give patterns closely resembling  $(5 \times 1)$ ,  $(2 \times 1)$  and  $(3 \times 1)$  respectively.

Intensity can be expected as fractional seventeenth orders with the two most intense extra spots having the proper splitting fraction  $F$ . Primitive calculations of the type carried out for  $(5 \times 1)$  show this unexpectedly well.

In figure 8 we give calculated intensity distributions for -BBBBBBBC-, -BCBCBCB- and -BCCCCC- with intensity for integral spots normalized to unity. These distributions strikingly resemble the appropriate patterns of Figure 5, where splittings close to the fractions  $1/17$ ,  $3/17$  and  $5/17$  can be seen in the first, fourth and seventh strips from the left. The calculations, though only qualitatively reliable, properly show the appropriate increase in splitting with increase in coverage, and also feature strong intensities only at the expected positions.

We can also use our model to illustrate the effect of cells constructed of B and C blocks but not having maximum homogeneity. We show this in Figure 9 where intensity distributions are compared for the three possible symmetric cells containing 10/17 of a monolayer of oxygen. These are -BCBCBCB-, -CBBCBBC- and -BBCCCBB- in order of decreasing uniformity. For the least uniform case -BBCCCBB- the calculated relative intensities bear no resemblance to what is experimentally observed, in contrast to those for -BCBCBCB-. This is evidence that the principle of uniformity plays an all important role in the development of the actual experimental superstructures.

We can imagine values of coverage for which ridiculously large unit cells would hypothetically be needed if the uniformity principle were in fact strictly followed. But such hypothetically large cells can be thought of as simpler sequences containing regularly repeating slight deviations. In reality these deviations would be much more random although the uniformity principle would still control the overall state of affairs. Hence the idea of very well ordered superstructures for large cells must break down, though superstructure spots will be still positioned as predicted by the relation between splitting fraction  $F$  and coverage  $\theta$ .<sup>14</sup>

## STREAKING

In what has preceded we have stressed the development of superstructures at 300°C. At room temperature, on the other hand, regular superstructures are not observed, and streaks in the patterns are generally observed between coverages for which long range order spontaneously develops at 30°C<sup>1-3</sup>.

When the clean Ni(110) surface is exposed to only 0.2L of oxygen, streaks become visible connecting  $hk$  and  $h+1,k$  spots. With more oxygen these streaks coalesce into the  $(3 \times 1) - 0[1/3]$  pattern of Figure 1B which is at its best at 0.5L. Then new streaks promptly develop, mainly in the region between the  $h+\frac{1}{3},k$  and  $h+\frac{2}{3},k$  positions, and at 0.8L these sharpen into the half-order spots of the  $(2 \times 1) - 0[1/2]$  pattern. More exposure at room temperature causes streaking to develop yet a third time, leading, as we have described, to the sharp  $(3 \times 1) - 0[2/3]$  pattern of Figure 2. We propose that all these streaks can be understood at any particular coverage in terms of structural composites. These have repeating atomic sequences of different lengths but of similar oxygen concentration. The inability to achieve at room temperature maximum homogeneity, which is the guiding principle for the formation of superstructures at 300°C, can be understood in terms of lower diffusion mobilities at 30°C.



Let us consider streaking at room temperature for coverage  $\theta$  between  $1/2$  and  $2/3$ . Streaks could be produced at given  $\theta$  by many sequences of differing length having values of  $R$  nearly the same. Short range order is presumed and these sequences are assumed to be made of the units B and C, though more non-uniform grouping of the atoms cannot be ruled out (see caption to Figure 9).

In similar fashion, streaking for coverage between  $1/3$  and  $1/2$  at room temperature can be assumed to arise from sequences composed of the units A and B, while streaking at coverages less than  $1/3$  could arise from isolated oxygen atoms separated by at least three spacings in the  $[110]$  surface direction.

Finally we mention that when  $O[1/3]$  has been clustered into patches of  $(2 \times 1)$  at  $300^\circ\text{C}$  (described at the beginning of this paper), cooling causes the quite sharp  $(2 \times 1)$  spots to become streaks. These coalesce into the normal  $O[1/3]$  pattern when the crystal is close to room temperature. Evidently while the  $(2 \times 1)$  islands are changing back to the homogeneous  $O[1/3]$  arrangement, different parts of the surface are covered by superstructures of differing composition and a combination of these produces the streaking as the crystal cools.

## REDUCTION BY HYDROGEN

A few observations upon the removal of oxygen from a (110) nickel face by heating in hydrogen are closely related to the experiments of the preceding section, and these will be given here. They represent only a small part of a careful study of oxygen-hydrogen reactions on a (110) face which is not yet completed. There are in addition two other common methods of removing oxygen. These are: (1) diffusion of oxygen into the crystal, which is effective only when there is very little oxygen in the interior, and (2) argon ion bombardment. The first of these is the subject of a study which is now also nearly finished.

The removal of oxygen by hydrogen takes place at 200°C and at higher temperatures<sup>15</sup>. In the tests reported here the crystal was maintained at 300°C in hydrogen at about  $1 \times 10^{-6}$  torr, with the gas flowing continuously through the experimental chamber. At intervals the crystal heating current was turned off for just a few seconds in order to photograph the diffraction pattern (always at 90 ev).

For the entire time the pattern was like those of Figure 5; there was always a pair of superstructure spots having a fractional separation lying between 0 and 0.33. This fraction  $F$  decreased continuously with hydrogen

exposure between these limits. Figure 10 gives measured values of  $F$  during a hydrogen exposure run as described. In this case the initial oxygen coverage was slightly less than two-thirds of a monolayer with the surface becoming clean at 650L of hydrogen. The diffraction pattern remained sharp for about the first 350L of  $H_2$  but then streaking began to develop in the region between the superstructure spots. Fractional order intensities also began seriously to weaken at this point. After 500L they were quite faint and the pattern was a somewhat weak and slightly streaked (2 x 1) resembling Figure 1C.

The decrease of  $F$  with increasing hydrogen exposure would suggest that the coverage is decreasing from  $2/3$  to  $1/2$ , corresponding to the behavior of  $F$  during oxygen exposure, the two processes being complementary to each other. But the superstructure spots decrease in intensity in the later stages, and only a very weak (2 x 1) is observed when  $F$  reaches zero. This means that the final coverage is close to zero, not  $1/2$ .

We suggest that during the first 350L or so of  $H_2$  the distribution of oxygen is quite uniform over the surface and that superstructures appropriate to a diminishing coverage are formed. After 350L this distribution apparently becomes less and less uniform as reduction proceeds. Uniform regions, where the coverage is still continuously decreasing, presumably become

gradually less important while new areas become increasingly enlarged in which coverages are considerably lower. This would account for the observed weakening of the superstructure spots accompanying an increasing development of streaking between them. Our observations suggest that in the last stages portions of the surface having coverages close to half a monolayer adjoin large areas in which the coverage is very dilute. This is consistent with the clustering phase transformation at  $300^{\circ}$  described in the first section of this paper.

On the basis of kinetic theory, the removal of  $2/3$  of a monolayer by hydrogen exposure of 650L represents a mean efficiency of  $9 \times 10^{-4}$ . This efficiency is known to be a strong function of the temperature of the crystal, but the nominal temperature of  $300^{\circ}\text{C}$  could not be carefully controlled during the experiment. The evidence we now have suggests that at an intermediate stage the efficiency is different at different places on the surface. Such an effect might be connected with surface structure, but extensive interpretation must await a better understanding of the oxygen hydrogen reaction.

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CAPTIONS

- Fig. 1 LEED patterns from a (110) nickel surface. 90 ev. A. Clean surface. Room temperature. B. After oxygen exposure of 0.4L at room temperature ( $2 \times 10^{-8}$  torr for 20 seconds). Crystal at room temperature during photograph. C. Same surface with crystal slowly cooling from 300°C during photograph (heat just turned off). D. After room temperature oxygen exposure of 0.8L. The usual sharp (2 x 1) pattern.
- Fig. 2 LEED pattern from a (3 x 1) structure produced by oxygen exposure of 5L.
- Fig. 3 Diffraction pattern at room temperature after oxygen exposure of 2.1L while crystal was at 300°C. 90 ev. Measured value of  $F = 0.17$ . Lined-off portion of photo shows region of pattern used in Figs. 5 and 6.
- Fig. 4 Plot of the splitting fraction  $F$  against oxygen exposure after the crystal had been exposed to different amounts of oxygen while held at 300°C.
- Fig. 5 Reproductions of portions of many of the photographs upon which Fig. 4 is based (see Fig. 3). 90 ev. Horizontal spacings are adjusted to be proportional to oxygen exposure. The linear increase of the fraction  $F$  with exposure is shown

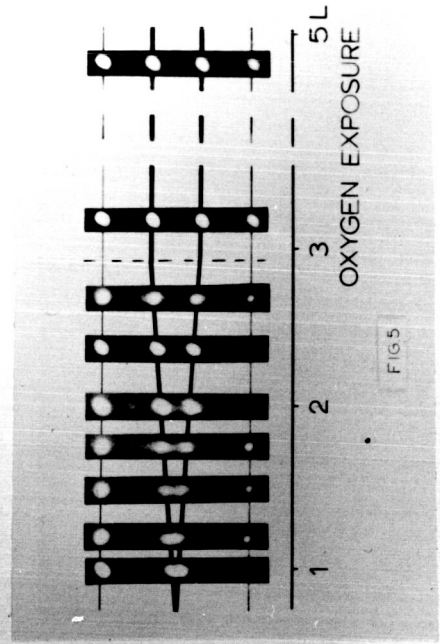
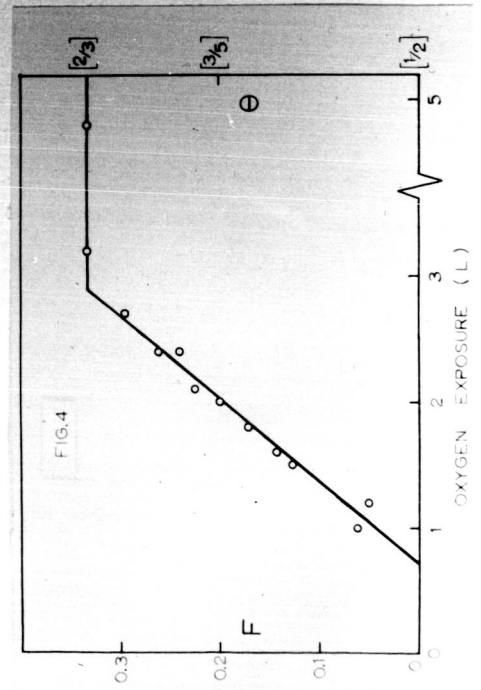
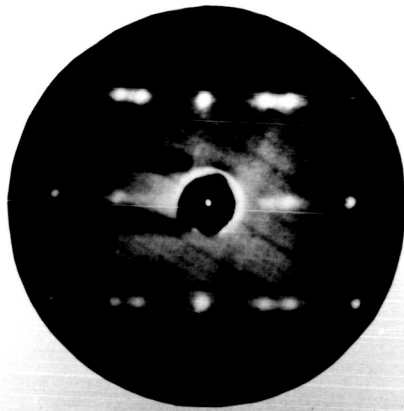
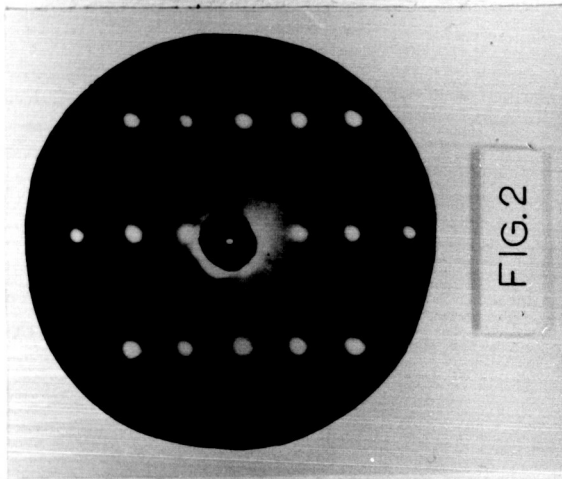
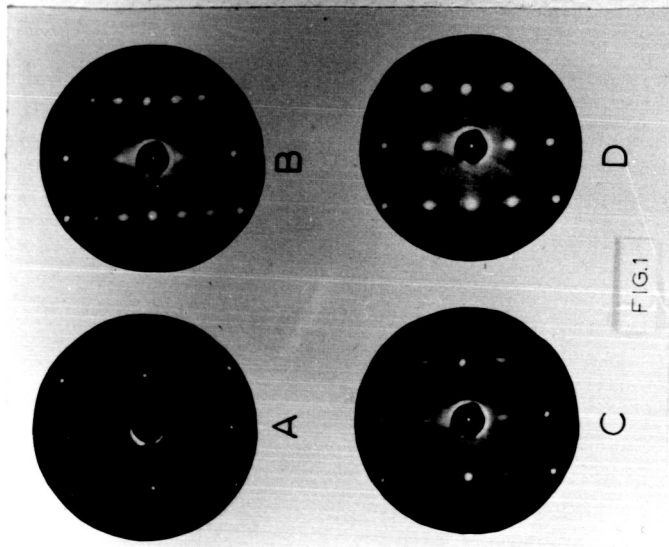
by the straight lines drawn between the photographs.

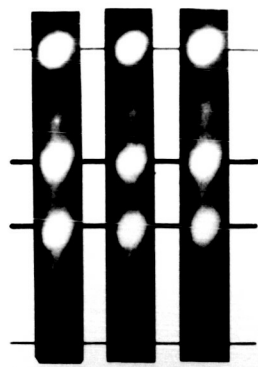
- Fig. 6 Sections of patterns at 90 ev (see Fig. 3) after crystal at 300°C given oxygen exposure of 1.8L. A. Immediately after oxygen valve shut. B and C. Same surface after heating further at 300°C for 30 and 150 seconds with oxygen valve shut.
- Fig. 7 Simplest case demonstrating the effect of short range order. Relative intensities calculated for two fundamentally different (5 x 1) structures (see text). A. Symbolic unit -ONiONiO-. B. Symbolic unit -NiOOONi-.
- Fig. 8 Calculated relative intensities at three coverages for ideal superstructures repeating every seventeen spacings in the [110] surface direction. A. Just over half a monolayer of oxygen ( $\theta = 9/17$ ) symbolized by -BBBBBBC- (see text). The calculated pattern is close to (2 x 1). B. Just under three-fifths of a monolayer ( $\theta = 10/17$ ) in the most uniform arrangement and symbolized by -BCBCBCB-. The calculated pattern is close to (5 x 1). C. Just under two-thirds of a monolayer ( $\theta = 11/17$ ) symbolized by -BCCCCC-. The calculated pattern is very nearly (3 x 1).



Fig. 9 Results of calculations comparing different degrees of uniformity within the cell for  $\theta = 10/17$  (see Fig. 8). These are three possible symmetric cells made of the blocks B and C (see text). A. The most uniform -BCBCBCB-. Calculated intensities are most similar to experiment. B. Less uniform -CBBCBBC-. C. The least uniform -BBCCBB-. Calculated intensities are very different to experiment with crystal at 300°C, but bear some resemblance to what is observed at room temperature.

Fig. 10 Plot of the fraction F against hydrogen exposure. Data obtained from photographs while crystal was being cleaned of oxygen at 300°C. Relation between F and  $\theta$  is no longer simple. At 650L of H<sub>2</sub> pattern was that of a clean surface. Filled circles indicate presence of streaking in region of pattern between main superstructure spots. Open circles represent superstructure patterns not having this streaking.





A B C

FIG.6

