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Low Energy Electron Diffraction Studies of Adsorbed Gases

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The adsorption of oxygen and hydrogen upon a clean (110) face of a nickel crystal has been studied by low energy electron diffraction. The arrangements of the adsorbed atoms or molecules are determined and the variations of these arrangements with time, temperature of the crystal, and pressure of the gas. During the formulation of the first monolayer the sticking probability is about unity for oxygen and about 0.05 for the formulation of hydrogen. Both gases cause diffusion of nickel atoms from the metal into the monolayer, even at room temperature, so that the monolayer is made up partly of nickel atoms and partly of the gas. Many complex structures can be produced within the fisrt monolayer of nickel and oxygen atoms, but only two nickel-hydrogen structures are known. Layers of amorphous oxygen and of amorphous hydrogen can be formed on top of the first monolayer.

Electrons of low energy back reflection diffraction patterns have been post accelerated by a potential difference of 4 kv, so that the pattern can be seen on a fluorescent screen and can be photographed¹⁾. Using this technique information has been obtained about the adsorbed atoms in the first monolayer upon surfaces of nickel crystals, and about the conditions under which these atoms will react with atoms of a different species subsequently admitted to the apparatus. The gases reported in this paper are oxygen and hydrogen. This report is limited to adsorption studies upon a (110) surface with brief reference to previously published studies upon the more dense (111) and (100) surfaces2),3).

Oxygen is adsorbed as atoms upon a clean (110) nickel face in a perfectly regular arrangement with a sticking probability of about unity, with the surface at room temperature or at elevated temperatures up to at least 600°C. The surface becomes covered by half of a monolayer of oxygen atoms before the sticking probability is significantly reduced. The interstices between oxygen atoms of this half layer are filled by nickel atoms which have diffused into the half layer from the bulk of the crystal or along its surface. This diffusion takes place even with the crystal at room temperature.

With further exposure molecular oxygen is adsorbed with a much lower sticking probability (~ 0.1) in what seems to be an amorphous structure on top of this first monolayer of mixed oxygen and nickel. Some of this oxygen is subsequently dissociated, slowly at room temperature and rapidly at 100°C, with oxygen atoms displacing some nickel atoms in the superficial layer and completely changing the arrangement of the remaining atoms.

These conclusions are drawn from the way in which the diffraction pattern on the fluorescent screen is observed to change. At first there is a relatively rapid development of sharp new diffraction spots corresponding to the monolayer in which half of the atoms are oxygen and half are nickel. This is followed by the much slower appearance of a bright haze over the entire pattern tending to obscure the sharp diffraction spots; the haze is attributed to oxygen molecules in an amorphous arrangement. Still later, and quite slowly at room temperature, the sharp diffraction spots, which represent the mixed monolayer, become streaked in one direction and then these diffused streaks become resolved into sharp spots in new locations. These first two patterns of sharp diffraction spots are not the same in all of our experiments. The patterns which occur most reliably are shown in Figs. 1a and 1b. Other patterns, corresponding to more complex structures, sometimes appear but will not be considered in this short paper⁴⁾.

The nickel atoms of the structures corresponding to the two patterns of Fig. 1 are shown schematically in the sketches of Fig. 2. Oxygen atoms, which are not shown, are presumed to lie between the nickel atoms of the superficial layer. We have referred these structures to rectangular A and B axes, respectively along the [100] direction which lies in the surface of the crystal and along the [011] surface direction which is normal to it. The structures represent spacings between surface nickel atoms in the B azimuth which are respectively double and triple the usual atom spacing. They have, therefore, been named the B2 structure, and the B3 structure. In the patterns of Fig. 1 the diffraction spots produced by these double and triple



(a)



(b)

Fig. 1. Diffraction patterns from which the surface structures of Fig. 2 are deduced. (a) Pattern from the B2 structure. (b) Pattern from the B3 structure.



Fig. 2. Sketches of nickel atoms of a (110) surface showing the superficial fractional layers of nickel atoms in the B2 structure (a) and in the B3 structure (b). Oxygen atoms, not shown, make up 0.5 of the surface layer in the B2 structure (Fig. 2a) and 0.67 of the surface layer in the B3 structure (Fig. 2b).

spacings are identified by fractional twodimensional Miller indices.

Interesting information is obtained from the way in which these oxygen structures can be removed by heat. The diffuse haze is dispelled by heating the crystal to 200°C, and from this we conclude that the amorphous molecular oxygen is vaporized from the surface at this relatively low temperature. A somewhat higher temperature, 350°C, causes the B3 structure to revert to the B2 structure, obviously with loss of one quarter of the oxygen in the superficial layer. The half layer of oxygen of the B2 structure is, however, exceedingly stable. It is not removed quickly by heating, up to temperatures at which rapid evaporation of nickel begins to occur. All of the complex structures formed by adsorbed oxygen atoms are, however, readily removed at 200°C when hydrogen is present.

With both oxygen and hydrogen present at the same time, the surface structure varies with temperature, time and partial pressures. A few significant observation have been made but complete two-dimensional phase diagrams have not yet been worked out.

In one type of experiment, we have carried through a series of transformations with temperature, at fixed oxygen and hydrogen pressures. An interesting set of conditions is one in which the hydrogen pressure is much greater than the oxygen pressure. For hydrogen pressures of the order of 1×10^{-7} mm

Hg and oxygen pressure less than one-tenth as great, temperatures have been varied cyclically from 200°C, to 25°C, to 100°C, to 200°C, etc. At 200°C the surface is comparatively clean*. At 25°C it has a superficial structure in which nickel atoms have a double spacing in the A azimuth but normal spacing in the Bazimuth-called the A2 structure. The intermediate sites in the A azimuth are presumed to be filled by hydrogen; it is now believed that water molecules are not responsible for the A2 structure because exactly the same structure is produced by hydrogen in the complete absence of oxygen, and after the same hydrogen exposure. At 100°C the surface is covered by the B2 structure.

Considerable information is furnished by the nature of the transitions between these three stable structures which occur when the temperature of the crystal is changed. On increasing the temperature from 25°C to 100°C, the diffraction spots characteristic of the A2 structure disappear instantly, leaving only the pattern of the planar structure. Then quite slowly new diffraction spots of the B2 structure begin to appear, at first very streaked and becoming gradually sharper. We conclude that hydrogen is evaporated from the crystal at once at 100°C. From the time required for the characteristic B2 diffraction spots to develop we can estimate the oxygen pressure on the assumption

* Evidence that it is never completely clean immediately after heating at 200°C is obtained by subsequent heating to a higher temperature. This later heating results in some increase in the brightness of the diffraction pattern. At the same time it produced an instantaneous rise in pressure by an amount which corresponds to a small fraction of a monolayer of adsorbed gas. that every oxygen molecule striking the surface is dissociated and sticks to the surface as two separate atoms. On raising the temperature to 200°C, the spots of the B2 structure disappear slowly (but more rapidly than they were formed) at a rate corresponding to the removal of an oxygen atom from the surface by every hydrogen molecule which strikes the surface in its immediate vicinity. The development of the A2 structure when the crystal temperature is lowered from 200°C to 25°C is also a slow transition corresponding to sticking probability of hydrogen of the order of 0.05. The A2 structure which is first formed at 25°C is, however, not strictly stable in the presence of even a very small concentration of oxygen. Even at 25°C it has been found to change in a few hours to the B2 structure, doubtless due to ultimate displacement of adsorbed hydrogen by oxygen. Much more work will be required to make these observations quantitative.

References

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