

## ION BEAM STUDIES OF OXYGEN EXPOSED Ni(100)

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A clean Ni(100) surface and a surface exposed to  $^{18}\text{O}_2$ , have been studied by high-energy ion scattering and nuclear reaction analysis. The structure of the clean and the exposed surfaces is studied by 750 keV  $\text{He}^+$  ion scattering in combination with channeling and blocking. The results are consistent with results obtained by medium-energy ion scattering. Absolute oxygen contents are measured using the  $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$  nuclear resonance at  $E_p = 1766$  keV. It is found that the oxygen content of the surface for which the  $c(2 \times 2)$  LEED pattern is observed, is  $0.42 \pm 0.04$  of a Ni(100) monolayer. The oxygen content of a saturated oxide layer is  $2.4 \pm 0.2$  of a monolayer. Furthermore, it is concluded that the saturated oxide layer consists of stoichiometric NiO.

### 1. Introduction

The reaction of oxygen with clean surfaces of nickel is one of the most widely studied subjects in the field of surface science [1]. Among the available experimental techniques, ion and atom scattering have proved to be useful [2–4], especially since they give real space information and are, in principle, quantitative.

The reaction sequence of oxygen with a Ni(100) surface has been postulated in 1970 by Fehler and Mott [5] and has been confirmed experimentally by, for example, Holloway and Hudson [6] using AES, by Mitchell et al. [7] using XPS and RHEED and by Smeenk [3] using ion scattering. Initially, the  $p(2 \times 2)$  and then the  $c(2 \times 2)$  LEED pattern is observed. After prolonged oxygen exposure, NiO starts to nucleate. The nucleation sites are a few monolayers thick and grow laterally until they coalesce and form a saturated, homogeneous nickel oxide layer with a thickness of two or three monolayers. At elevated temperatures, the nickel oxide layer slowly thickens [8].

It is generally found that the Ni(100) surface is not reconstructed during oxygen chemisorption [3,8]. Medium-energy ion scattering measurements by Frenken et al. [4] have shown that, during chemisorption, the small inward relaxation of the outermost crystal layer of the clean surface is changed into an outward relaxation.

There exists, however, conflicting values for the exact oxygen coverage in the  $c(2 \times 2)$ -O chemisorbed phase. The LEED pattern suggests a coverage of half a monolayer. Frenken et al. [4] have measured a coverage of  $0.46 \pm 0.04$ . On the other hand, Holloway et al. using AES [6], Mitchell et al. using RHEED and XPS [7], Norton et al. using XPS [9] and Smeenk using medium-energy ion scattering [3] have measured an oxygen coverage of only  $0.33 \pm 0.03$  of a monolayer.

In the present study the reaction of oxygen with a Ni(100) surface is investigated with MeV ion beams ( $H^+$  and  $He^+$ ). In particular, the structure of a clean and an oxygen exposed (i.e. the  $c(2 \times 2)$ -O) Ni(100) surface, is analyzed. Using the technique of CHABLIS (channeling and blocking of ions in surfaces), structural information is obtained by varying the direction of the incident beam or that of the detected beam while keeping the direction of the other beam fixed. Absolute oxygen coverages are determined by nuclear reaction analysis (NRA).

## 2. Experimental methods

The (100) surface of a nickel crystal is cleaned by repeated cycles of 750 eV  $Ar^+$  sputtering and annealing at 800 K. After the cleaning procedure, the  $(1 \times 1)$  LEED pattern of the clean Ni(100) surface is observed. Enriched oxygen (99%  $^{18}O$  and 1%  $^{16}O$ ) is introduced into the vacuum system at a pressure of about  $10^{-4}$  Pa. The oxygen adsorption on the nickel surface is monitored by AES. The UHV system in which all experiments are performed, is described in detail in ref. [10].

In two different experiments the surface is exposed to 100 L ( $1.33 \times 10^{-2}$  Pa s) at a crystal temperature of 600 K, and to 300 L ( $4 \times 10^{-2}$  Pa s) at 350 K. In the former case the  $c(2 \times 2)$  LEED pattern, and in the latter a diffuse, hexagonal LEED pattern is observed. The AES measurements agree qualitatively with the reaction sequence as described in the introduction, in particular with the measurements by Mitchell et al. [7] and by Smeenk [3]. After the 300 L exposure a saturated nickel oxide layer is formed.

The ion beam measurements are performed with the clean, the oxygen covered ( $c(2 \times 2)$ -O) and the oxidized nickel surface. During the CHABLIS measurements, the detector is aligned with the  $[1\bar{1}0]$  crystal axis. Consequently, ions backscattered in the second or a deeper crystal layer into the direction of the detector, are partially blocked by the  $[1\bar{1}0]$  atomic rows. Angular scans are performed by varying the direction of the incident beam of 750 keV  $He^+$  within the (001) crystal plane, between a scattering angle of  $84^\circ$  and of  $96^\circ$ . Note that at a scattering angle of  $90^\circ$  the incident ion beam is aligned with the  $[110]$  crystal axis. The energy resolution of the detector is 12 keV (FWHM), the angular resolution is  $1.2^\circ$ . The beam dose per scan,

measured by target current integration, is 250  $\mu\text{C}$ . The angular spread of the incident beam is about  $0.1^\circ$ .

In addition, some spectra are measured under random-incidence and -detection conditions. They will be used for the normalization of the CHABLIS spectra.

The  $E_p = 1766$  keV resonance of the  $^{18}\text{O}(p, \alpha)^{15}\text{N}$  nuclear reaction is used for NRA. An accurate value for the cross section of this resonance will be published elsewhere [11].

### 3. Experimental results

Fig. 1 shows energy spectra of 750 keV  $\text{He}^+$  ions which are backscattered from the clean Ni(100) crystal under random-incidence and -detection conditions, under single-alignment conditions (i.e. only blocking), and under double-alignment conditions (channeling and blocking). The large reduction in the

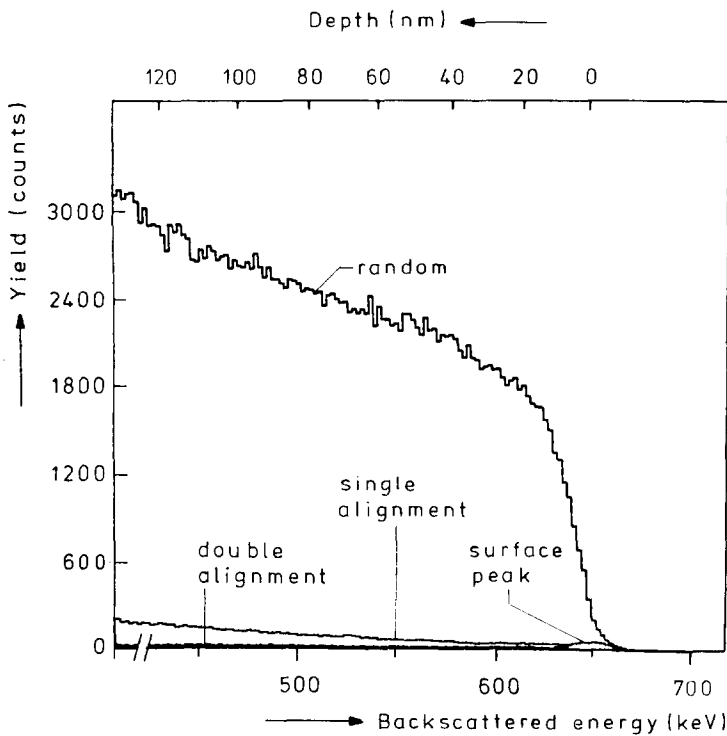


Fig. 1. Random, single-alignment and double-alignment spectra of a clean Ni(100) crystal. Analysis of the content of the surface peak, as a function of the direction of the incident beam, reveals structural information about the surface.

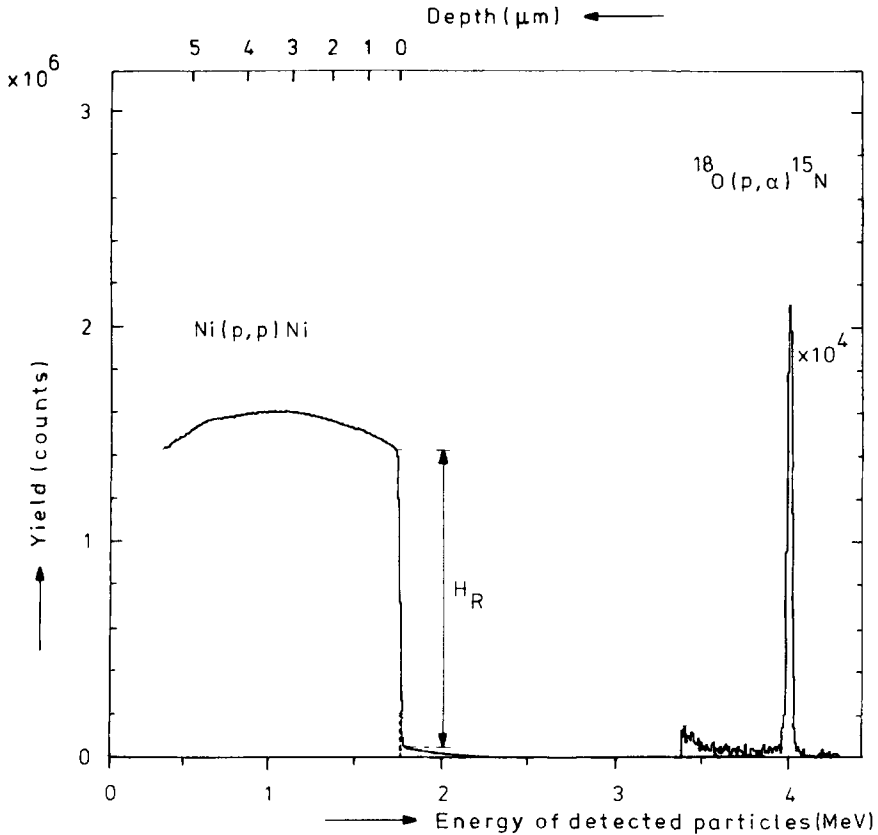


Fig. 2. Typical NRA spectrum of the  $c(2 \times 2)$ - $^{18}\text{O}$ -Ni(100) crystal. At 3.94 MeV the  $(p, \alpha)$  peak is clearly visible. Note also the large difference between the number of elastically backscattered protons and the number of  $\alpha$ -particles. The height  $H_R$  is used for spectrum normalization.

number of detected ions, especially under double-alignment conditions, is evident. A small peak, caused by backscattering at the very surface of the crystal, is visible in the single- and the double-alignment spectra. The spectra of the oxygen exposed crystal are qualitatively similar. The number of ions backscattered from oxygen is in all cases too low to observe an oxygen peak in the CHABLIS spectra.

A typical NRA energy spectrum is shown in fig. 2.

#### 4. Analysis of the spectra

The content of the surface peak, usually expressed in number of visible atoms per row, as a function of the scattering angle, reveals information about

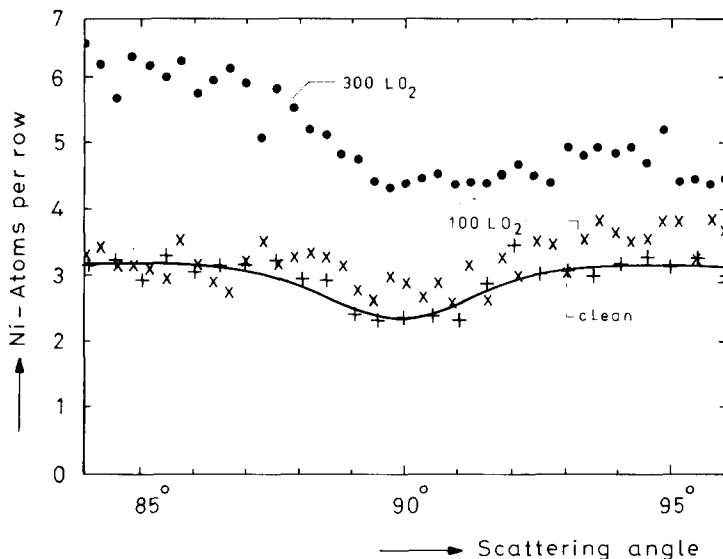


Fig. 3. Angular scans of the normalized content of the surface peak of the clean surface (+); the  $c(2 \times 2)$ -O surface (x); and the oxidized surface (●). The full curve is the result of the Monte Carlo simulation which fits best the measurement of the clean surface.

the structure of the very surface [12]. The content of the  $^{18}\text{O}(p, \alpha)^{15}\text{N}$  peak in a NRA spectrum reveals, by comparison with the height  $H_R$  in the  $\text{Ni}(p, p)\text{Ni}$  spectrum [10], the absolute oxygen coverage.

Fig. 3 shows scans of the content of the surface peak. The uncertainty, which is mainly determined by the method of background subtraction [10] and by the measurement of the relative beam dose, varies between 8 and 15%.

The angular scans show a dip around the direction for which the incident beam is aligned with the [110] crystal axis. The exact scattering angle is calculated by using, as reference, the position of the minimum in the yield of particles backscattered in the bulk. The minima of the dip in fig. 3 are located at  $90.0^\circ \pm 0.25^\circ$  and at  $90.25^\circ \pm 0.25^\circ$  for the clean and the  $c(2 \times 2)$ -O surface, respectively.

The angular scan of the  $c(2 \times 2)$ -O surface is shifted upwards over about  $0.4 \pm 0.2$  nickel atoms per row, as compared to the scan of the clean surface. The shift suggests an increase in the vibration amplitude of the nickel atoms in the first layers or some disorder at the surface. The scan of the oxidized surface is shifted upwards over  $2.3 \pm 0.5$  nickel atoms per row.

The oxygen coverage in the  $c(2 \times 2)$ -O phase is, according to NRA,  $(0.68 \pm 0.07) \times 10^{15}/\text{cm}^2$ , corresponding to  $0.42 \pm 0.04$  of a Ni(100) monolayer. The oxygen content of the saturated oxide layer is  $(3.8 \pm 0.3) \times 10^{15}/\text{cm}^2$ , corresponding to  $2.4 \pm 0.2$  monolayers, being equal to the additional number

of visible nickel atoms per row. Apparently, the oxide layer consists of stoichiometric NiO.

The angular scans of the clean and of the  $c(2 \times 2)$ -O surface are analyzed further by use of Monte Carlo computer simulation of the CHABLIS experiment [10]. In the simulation, the vibration amplitude of atoms in the first crystal layer and the relaxation of the first interlayer spacing are varied. It is therefore assumed that the  $c(2 \times 2)$ -O surface is neither reconstructed, nor disordered. The value of the vibration amplitude of the atoms in the second layer is assumed to be the mean of the bulk (i.e. 8.4 pm [13]) and the first-layer value.

Optimal agreement between the results of the measurement of the clean surface and of the calculation – the solid curve in fig. 3 – is obtained when assuming a vibration amplitude of  $11.5 \pm 2.5$  pm and a relaxation of  $0\% \pm 4\%$ . The figures for the  $c(2 \times 2)$ -O surface are  $14.0 \pm 2.5$  pm and  $+3\% \pm 4\%$ , respectively.

## 5. Summary and discussion

CHABLIS using a 750 keV  $He^+$  ion beam, is applied to study clean and oxygen covered Ni(100) surfaces. Information about the structure of the outermost surface layer is obtained by aligning the detector with a  $[1\bar{1}0]$  crystal axis and by varying the direction of the incident beam around the  $[110]$  axis. By comparison with Monte Carlo simulation, a value of  $0\% \pm 4\%$  for the relaxation of the first interlayer spacing of the clean Ni(100) surface is found. The vibration amplitude of the atoms in the first layer is  $11.5 \pm 2.5$  pm.

From our measurement it is not clear whether the  $c(2 \times 2)$ -O surface is reconstructed, is slightly disordered or whether the vibration amplitude of the nickel atoms in the outermost crystal layers is enhanced. When no reconstruction or disorder is assumed, it is found that the outward relaxation of the first layer is  $3\% \pm 4\%$ , and the vibration amplitude of the nickel atoms in this layer is  $14.0 \pm 2.5$  pm.

The oxygen coverage of the  $c(2 \times 2)$ -O-Ni(100) surface is determined by NRA. A coverage of  $(0.68 \pm 0.07) \times 10^{15}/\text{cm}^2$ , corresponding to  $0.42 \pm 0.04$  of a monolayer, is found. The oxygen content of a saturated oxide layer is  $(3.8 \pm 0.3) \times 10^{15}/\text{cm}^2$ .

Our results for the relaxations and the vibration amplitudes are in good agreement with results of measurements by Frenken et al. [4] using CHABLIS with an intermediate-energetic ion beam. However, the uncertainty in our measurements is appreciably larger. Furthermore, since the duration of our CHABLIS measurements is rather long, some carbon contamination of the clean surface could not be avoided. It is noted that in the CHABLIS measurements by Smeenck [3] and Frenken et al. [4], not the direction of the

incident beam but that of the detector is varied. However, because of the reversibility of all scattering processes, both procedures are equivalent.

The oxygen coverage in the  $c(2 \times 2)$ -O phase found in our study by NRA, is in agreement with the result obtained by Frenken [4] but not in agreement with measurements by others [3,6,7,9]. Mitchell et al. [7] have measured the oxygen content of a saturated NiO layer, too. A value of  $3.3 \times 10^{15}/\text{cm}^2$  is found, which is somewhat lower than the value found in our study. In the measurements by the above mentioned authors [3,6,7,9] complicated calibration procedures had to be applied. Nuclear reaction analysis, on the other hand, directly reveals absolute oxygen coverages.

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