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M. Gautier  
*C.E.N. Saclay*

J. P. Duraud  
*C.E.N. Saclay*

J. P. Vigouroux  
*C.E.N. Saclay*

C. Le Gressus  
*C.E.N. Saclay*

R. Shimizu  
*Osaka University*

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OXIDATION OF ALUMINUM STUDIED BY ION SCATTERING SPECTROSCOPY (I.S.S)  
IN A SCANNING AUGER MICROSCOPE

M. Gautier, J.P. Duraud, J.P. Vigouroux, C. Le Gressus, R. Shimizu\*

Département de Physico-Chimie, C.E.N. Saclay  
91191 GIF SUR YVETTE, FRANCE

\* Department of Applied Physics, Faculty of Engineering,  
Osaka University, Suita-Shi, Yamada-Oka 2-1  
Osaka 565, Japan

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Abstract

The set up of an ion gun, producing a focused beam in the analysis chamber of a Scanning Auger Microscope permits ion scattering experiments: surface studies performed by electron spectroscopies can then be enlarged by Ion Scattering Spectroscopy (I.S.S.) to get additional information.

I.S.S. appears to be very sensitive to the cleanliness of the surface: comparison between Electron Energy Loss Spectroscopy (E.E.L.S.) and I.S.S. studies on clean samples show that I.S.S. can still detect oxygen even when it is not detectable by E.E.L.S.

Preliminary results on oxidation of Al (111) and Al (100) give oxidation curves in good agreement with those obtained by Auger Electron Spectroscopy (A.E.S.) and X Ray Photoemission Spectroscopy (X.P.S.).

Key Words: Scanning Auger Microscope, Electron Energy Loss Spectroscopy, Ion Scattering Spectroscopy, Oxidation of Aluminum.

\*Address for correspondence:

M. Gautier  
DPC/SSS-CEN Saclay,  
91191 GIF SUR YVETTE Cedex,  
FRANCE  
Phone n°: (6) 908-53-36

Introduction

Surface analysis methods currently available in a Scanning Auger Microscope are electron spectroscopies, such as Auger Electron Spectroscopy (A.E.S.), Electron Energy Loss Spectroscopy (E.E.L.S), Secondary Electron Spectroscopy (S.E.S.).

The set up of an ion-gun producing a focused beam in the analysis chamber permits ion scattering experiments in the Scanning Microscope: surface studies performed by electron spectroscopy can then be enlarged by I.S.S. (Ion Scattering Spectroscopy) to get additional information [5].

In this paper, sensitivity of E.E.L.S. and I.S.S. to the cleanliness of the Al surface is first discussed. Preliminary I.S.S results on the oxidation of Al (111) and Al (100) are compared with those obtained by electron spectroscopies.

Ion Scattering Spectroscopy (I.S.S):  
Physical basis and experimental set-up

Ion Scattering Spectroscopy deals with the study of the energy distribution of rare gas ions ( $\text{He}^+$ ,  $\text{Ne}^+$  or  $\text{Ar}^+$ ) which have been scattered from a solid surface.  
Physical basis

A binary collision model is applied to a collision between an incident ion (with  $M_1$  mass,  $E_0$  kinetic energy) and a target atom at rest (with  $M_2$  mass, kinetic energy 0) (Figure 1).

The incident ion is taken to be scattered with  $E_1$  energy, at a  $\varphi$  angle with respect to the direction of the incident beam, and transfers to the target atom a recoil energy T:

$$T = E_0 - E_1 = \frac{4M_1M_2}{(M_1 + M_2)^2} \sin^2 \frac{\varphi}{2} \quad (1)$$

$$\text{where } \tan \varphi = \frac{M_2 \sin \theta}{M_1 + M_2 \cos \theta}$$

The energy of the ion after collision is therefore:

$$E_1 = E_0 \left[ 1 - \frac{4M_1 M_2}{(M_1 + M_2)^2} \sin^2 \frac{\theta}{2} \right] \quad (2)$$

$$= f(M_1, M_2, E_0, \varphi)$$

The  $\varphi$  angle is determined by the detection geometry and  $E_0$  and  $M_1$  are known. Then the energy distribution of the ions emitted from the sample under ion bombardment is expected to show a maximum intensity for every energy  $E_1$  corresponding to any atom of mass  $M_2$  being present on the surface.

As for low primary energy ions, their penetration depth is small, so this spectroscopy is very sensitive to the outermost layer of the sample and, therefore, particularly interesting for studying gas adsorption on a solid surface.

#### Experimental set-up

An ion gun (Minibeam II of 3M) was fitted in the analysis chamber of a Scanning Auger Microscope (JEOL, JAMP 10) as depicted in Figure 2. The diameter of the impact spot of the  $\text{He}^+$  ion beam on the sample was less than 1 mm. This apparatus was also equipped with an  $\text{Ar}^+$  ion gun allowing the cleaning of the surface by ion etching.

Energies of secondary ions emitted by the solid surface and  $\text{He}^+$  ions scattered from the surface were analyzed through a cylindrical mirror analyzer (C.M.A.). The outer cylinder of the C.M.A. was positively biased, so that energy filtering of positive ions could be realized [3].

A slit was set between sample and analyzer in order to reduce the broad acceptance angle of the C.M.A. to a given  $\varphi$  angle (Figure 3). The angle of incidence of primary  $\text{He}^+$  ions with respect to the sample normal was then  $56^\circ$ , whereas the detection angle, as depicted on Figure 3, was  $116^\circ$ .

Detecting the  $\text{He}^+$  ions at the output of the C.M.A. could be realized by two modes: either synchronous detection with a lock-in amplifier ( $E \cdot dN(E)/dE$  distribution) or counting mode ( $E \cdot N(E)$  distribution).

#### Experimental

The base pressure of the analysis chamber was of about  $2 \times 10^{-7}$  Pa. It increased to  $2.10^{-5}$  Pa during the recording of an I.S.S. spectrum, due to helium pressure in the chamber.

Two Al samples (diameter 8 mm, thickness 1 mm) have been studied:

1) Al (100) monocrystalline, 2) polycrystalline Al sample, constituted of large grains with (111) orientation. They were prepared in the same way, both mechanically and electrochemically polished.

#### Cleaning of the sample

Al (100): The sample was heated to  $500^\circ\text{C}$  and ion etched (cycles of 10 min, Ar pressure in the chamber  $4 \times 10^{-3}$  Pa). After each ion etching cycle, an E.E.L.S. spectrum was recorded (with primary electron energy  $E_p = 250$  eV). The sample was considered clean when the energy loss peaks corresponding to the excitation of bulk plasmon (BP) and surface plasmon (SP) were found well defined, and their intensity ratio SP/BP was the most intense (Figure 4). This represents the most sensitive criterion of cleanliness currently used in a Scanning Auger Microscope [4].

Under these conditions, an I.S.S. spectrum was recorded (Figure 5). The ratio  $h_O/h_{Al}$  ( $h_O$  and  $h_{Al}$  represent respectively the peak to peak intensity of O and Al) was then about 5 %.

Al (111): The sample was heated to  $500^\circ\text{C}$  and ion etched (with the same conditions as for Al (100)). After each ion etching cycle, an I.S.S. spectrum ( $\text{He}^+$  ions, with primary energy  $E_0 = 1500$  eV) was recorded. When the ratio  $h_O/h_{Al}$  reached a constant value, the sample was considered clean. The evolution of the ratio  $h_O/h_{Al}$  versus sputtering time is plotted on Figure 6. The I.S.S. spectrum obtained on the clean polycrystalline sample (with large grains (111)) is given on Figure 7 ( $h_O/h_{Al} = 1.8$  %).

#### Oxidation of Aluminum

The clean surface of each sample was submitted to different oxygen exposures ranging from 0 Langmuir to 160 Langmuir. A 1 Langmuir exposure corresponds to an oxygen pressure of  $10^{-6}$  Torr during 1 second.

For every exposure, an I.S.S. spectrum was recorded, with primary ion energy  $E_0 = 1500$  eV. The ratio  $h_O/h_{Al}$  measured on each I.S.S. spectrum is plotted on Figure 8 as a function of oxygen exposure, for both Al (111) and Al (100). Figure 9 shows the I.S.S. spectrum obtained on Al (111) for a 100 L oxygen exposure.

#### Discussion

##### Cleanliness of the surface

During the cleaning, the ratio  $h_O/h_{Al}$  decreases with etching time and then becomes steady. For the polycrystalline (111) sample,  $h_O/h_{Al}$  is around 1.8 %. As this ratio was the smallest we could get, we considered this order of magnitude our criterion of cleanliness. Cleaning the Al (100) sample according to the usual plasmon test gives a ratio  $h_O/h_{Al}$  of only 5 %.

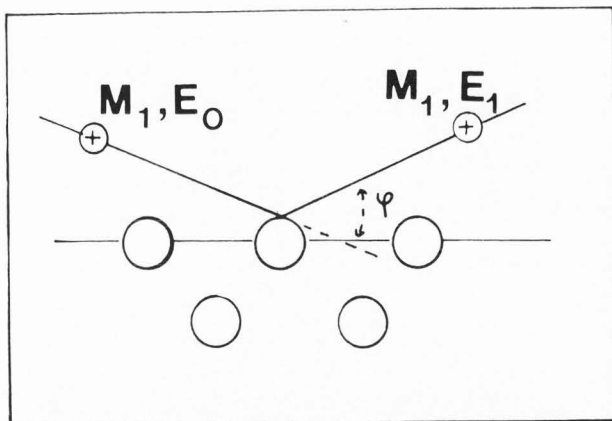


Fig.1. Binary collision between an incident ion (with  $M_1$  mass,  $E_0$  energy) and a target atom at rest (with  $M_2$  mass, energy 0).

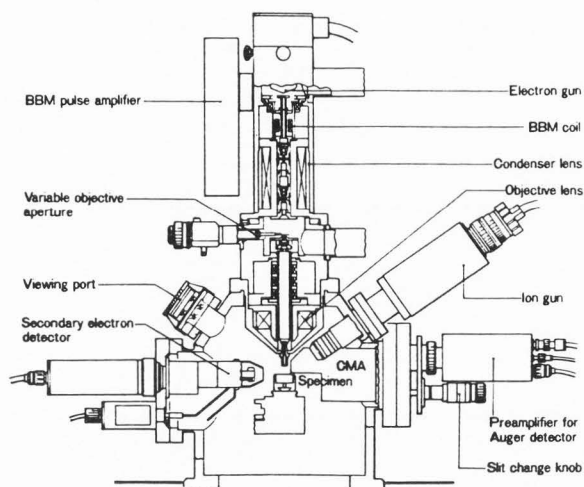


Fig.2. Scanning Auger Microscope JEOL (JAMP 10) (BBM = beam blanking modulation).

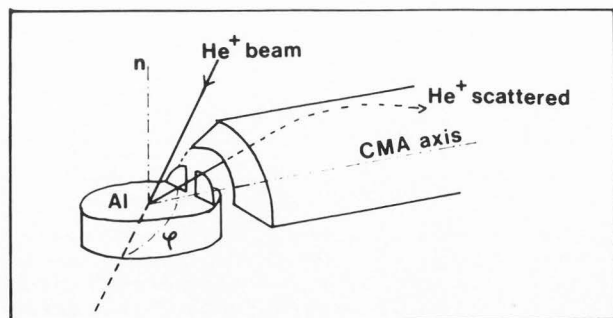


Fig.3. Detection set-up geometry.

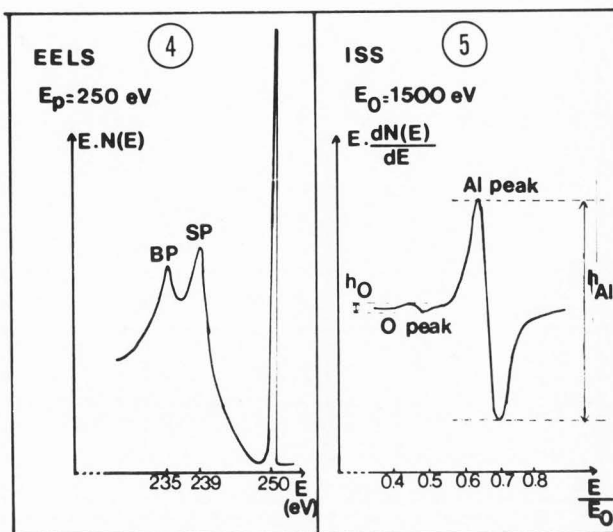


Fig.4. E.E.L.S. spectrum on clean Al(100) SP = surface plasmon, BP = bulk plasmon.

Fig.5. I.S.S. spectrum on Al (100)  $h_O/h_{Al} \approx 5\%$ .

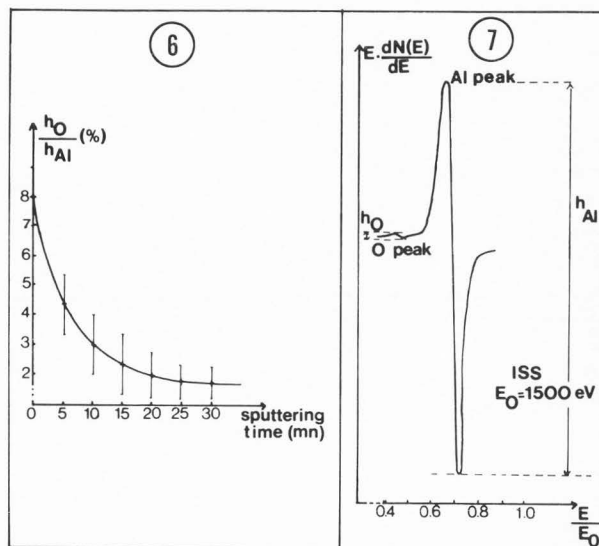


Fig.6. Evolution of the ratio  $h_O/h_{Al}$  as a function of sputtering time (5  $\mu$ A, 3 keV).

Fig.7. I.S.S. spectrum on clean Al (111)  $h_O/h_{Al} \approx 1.8\%$ .

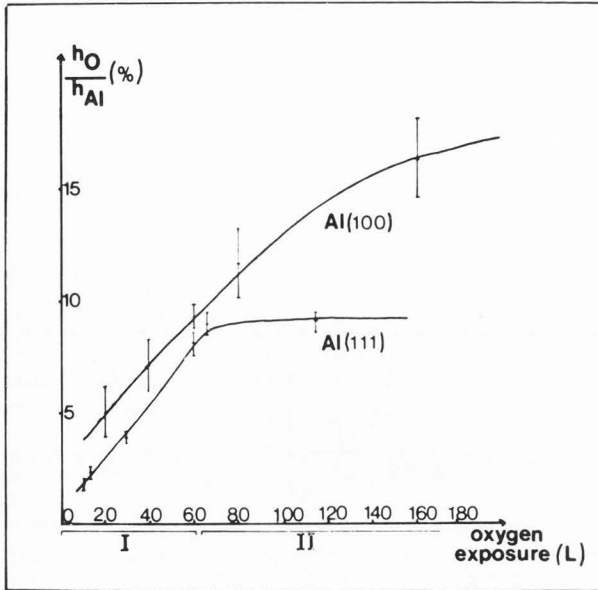


Fig. 8. Evolution of the ratio  $h_O/h_{Al}$  on Al (111) and Al (100) as a function of oxygen exposure.

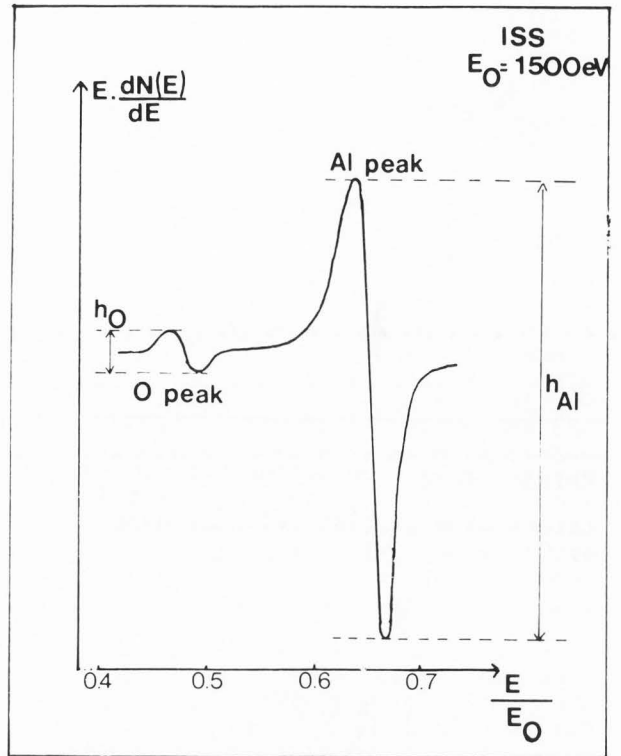
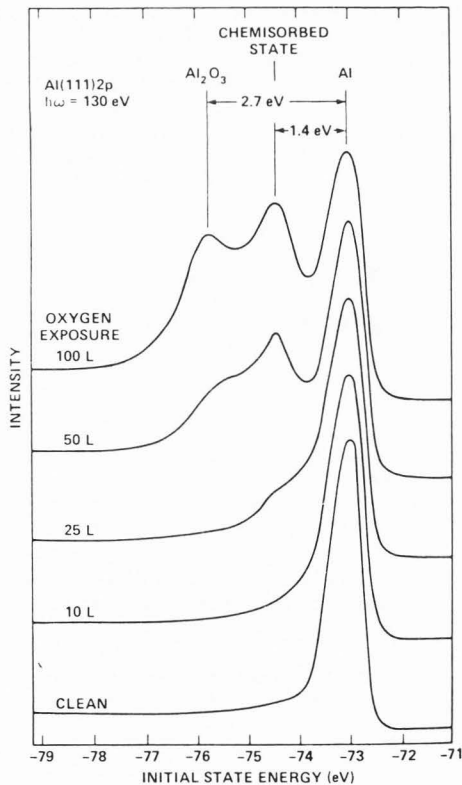
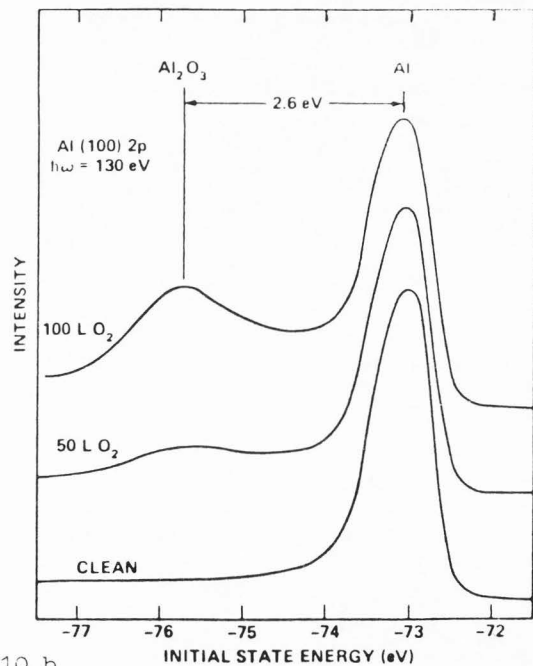


Fig. 9. I.S.S. spectrum (111), for a 100 L  $O_2$  exposure  $h_O/h_{Al} \approx 8\%$ .



10 a



10 b

Fig. 10. Spectra of the  $Al_{2p}$  core region as a function of oxygen exposure measured at an excitation energy of 130 eV (after [1]).  
a) for the (111) face,  
b) for the (100) face.

Comparison between E.E.L.S. and I.S.S. studies on clean samples shows that I.S.S. can still detect oxygen even when it is undetectable by E.E.L.S. (Figure 4). This shows the great sensitivity of I.S.S. to the surface since the ratio  $h_O/h_{Al}$  can vary from 1.8 % to 5 % without any change on the E.E.L.S. spectrum.

#### Oxidation of aluminum

The ratio  $h_O/h_{Al}$  increases as a function of oxygen exposure for both sample orientations (Figure 8). The Al (111) oxidation curve can be divided into two regions: in region I (0L-60L) the rate of increase of  $h_O/h_{Al}$  is larger than in region II (60L-100L). On the other hand, the increase on the Al (100) oxidation curve is continuous from 0L to 100L. These different behaviors of the oxidation curves on Al (111) and Al (100) can be related to the difference in the oxidation mechanisms between Al (111) and Al (100).

Photoemission studies [1] and low electron energy diffraction results [2] show that on the Al (111) face, low oxygen exposures (< 50L) lead to the creation of a chemisorbed state without oxygen incorporation. A peak, located 1.4 eV below the Al2p photoemission peak accounts for this chemisorbed state. For higher oxygen exposures (> 50L), a new structure appears, located 2.7 eV below the Al2p photoemission peak: it corresponds to the ionic bond Al-O, and to formation of Al<sub>2</sub>O<sub>3</sub> oxide (Figure 10). Region I could therefore be attributed to the chemisorption stage (strong increase of  $h_O/h_{Al}$ ), and region II to the oxide formation (weaker increase).

On the contrary, for the Al (100) face, the peak corresponding to the ionic Al-O bond appears even at low oxygen exposures (Figure 10). No structure appears that could account for a chemisorbed state, so that oxygen is directly incorporated into aluminum. This could explain the continuous behavior of the oxidation curve for Al (100).

Oxidation of low index-single crystal faces of aluminum has already been studied by AES [2]. The oxygen uptake is monitored by the O KLL peak intensity [2] (Figure 11). These oxidation curves display a similar behavior as those obtained by I.S.S.: continuous increase on Al (100) and a two step increase for Al (111) in the intensity of the O KLL Auger peak.

On Figure 11, the break in the shape of the O KLL curve appears for about 150L, whereas it appears for about 60L in the shape of the  $h_O/h_{Al}$  curve (Figure 8). This difference can be due to a different preparation of the samples in the two experiments or to radiation damage, different for A.E.S. and I.S.S.

On Figure 8, the absolute values of the ratio  $h_O/h_{Al}$  on Al (100) and on Al (111) cannot be compared because both curves do not have the same origin: Al (111) was cleaner than Al (100). Further experiments are required to confirm the break value for Al (111), and to have the same cleanliness of both samples in order to precisely calculate the part of radiation damage in I.S.S. measurements.

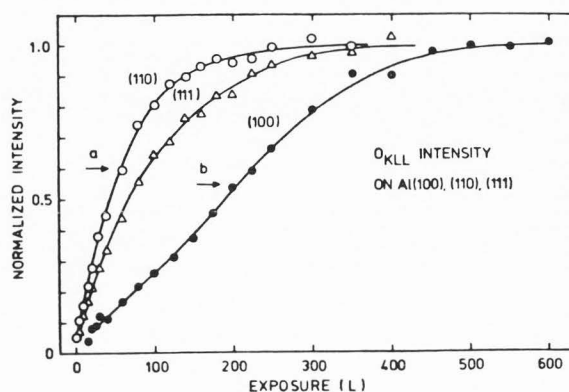


Fig.11. Intensity change for the O.K.L.L. peak on the (100), (110) and (111) crystal faces as a function of oxygen exposure (after [2]). Similar curves are also obtained by monitoring the O1s photoemission peak [2].

#### Conclusion

By simple arrangement of a Scanning Auger Microscope, I.S.S. measurements can be combined with A.E.S. under the same conditions. Moreover I.S.S. appears to be very sensitive to surface cleanliness. Preliminary results on oxidation of Al (111) and Al (100) allowed us to get oxidation curves in good agreement with those obtained by X.P.S. and A.E.S.

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#### Discussion with Reviewers

T.J. Shaffner: You mention that absence of the chemisorption mechanism is responsible for the steadily increasing nature of the Al (100) curve in Figure 8. Why then does not the Al (111) curve above 100L where chemisorption is absent, also steadily increase?

Authors: Oxidation mechanisms for Al (100) and Al (111) are well known [2]: chemisorption for low oxygen exposure on Al (111), followed by incorporation; and direct incorporation of oxygen into Al (100). This lead us to relate the two-step increase of Figure 8 for Al (111) and one step increase for (100) to these mechanisms. Further points are required on the (111) curve above 120L, in order to precisely determine the shape of the curve in this region.

Nevertheless, oxidation curves obtained by I.S.S. (Figure 8) display the same behaviour as those obtained by Auger (Figure 11): on Figure 11, the intensity for (111) above 300L remains steady, whereas for (100) it reaches a constant value above 400L; on Figure 8, the intensity for (111) reaches a constant value above 60-80L, whereas for (100) it remains steady above 180L. Only the break value is different, which can be due, as mentioned in the text, to a different preparation of the samples in the two experiments or to radiation damage difference for A.E.S. and I.S.S.

T.J. Shaffner: Does the curve in Figure 6 ever go to zero? If not, why not?

Authors: It should theoretically go

to zero. But the ratio  $h_O/h_{Al} = 1.8\%$  was the smallest we could get: this can be due to radiation damage induced by the incident ion beam, because of the rather-high primary energy (1500 eV).

T.J. Shaffner: You have emphasized the ratio  $h_O/h_{Al}$  in your work. Is there any significance to the changes in  $E/E_0$  between Figures 5, 7 and 9?

Authors: No there is no significance to the changes in  $E/E_0$ , they are only due to a change in scale of the  $E/E_0$  axis.

T.J. Shaffner: Figure 11 suggests that the (110) data resemble (111). Do you have corresponding data for  $h_O/h_{Al}$  for the (110)?

Authors: Unfortunately we don't.

W. Heiland: For a comparison with other ISS-work a representation of the experimental data in  $N(E)$  vs  $E/E_0$  would be helpful (e.g. in text ref. D.P. Smith, 1971).

Authors: Unfortunately we didn't have the experimental data in  $N(E)$  mode.

R. Holm: Did you observe multiple scattering effects under your experimental conditions to study the geometrical arrangement of the O-atoms on the Al-surface?

Authors: We could not vary the incidence angle at our disposal, so we could not study the geometrical arrangement of the O atoms on the Al surface, and the resolution we get did not allow us to study multiple scattering.

R. Holm: The authors state that ISS is more sensitive than other techniques to detect surface contamination. This may be true for certain elements especially in comparison to EELS. But it is well known that ISS is very insensitive with respect to hydrocarbons. What is your experience with your special instrument?

Authors: As yet, we have no experience on the sensitivity of ISS to hydrocarbons.