# Electron Induced X-Ray Emission Spectroscopy as a Method for Interface Study

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# ELECTRON INDUCED X-RAY EMISSION SPECTROSCOPY
## AS A METHOD FOR INTERFACE STUDY

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## Abstract

It is shown that from X-ray emission spectroscopy induced by electrons having appropriate kinetic energy, it is possible to analyze the valence electron distribution of solid/solid interfaces with a resolution equal to a few Å. Ni 3d states are obtained for metal/metal (Ni/Al) and metal/insulator (Ni/MgF$_2$ and Ni/SiO) interfaces. The structure of the interface, i.e. whether it is steep or diffuse can be determined. Chemical bonding between atoms in contact , when it exists, is evidenced. The method can be applied to systems such as they are encountered in fields like adhesion and microelectronics. The only limitation is that the element,which is studied in one of the materials in contact,must not be a constituent of the other material.

## Introduction

The valence electron distributions at solid/solid interfaces provide information concerning interactions on an atomic scale so that studying them should prove to be useful in various fields such as metallurgy, adhesion, microelectronics.

The non destructive methods mostly employed for the analysis of electron distributions are electron spectroscopies. These methods are very convenient for systems involving adatoms or very thin layers deposited on a surface and as a consequence for interfaces just formed; see for example: Kobayashi et al. (1980), Grunthaner et al.(1981),Franciosi et al.(1982), Chang and Erskine (1983), Nguyen and Cinti (1983), Tung et al. (1983), Calliari et al (1984), Kendelewiez et al. (1984), Petro et al. (1984), Abbati et al. (1985), Azizan et al. (1985), Lindau et al.(1985), Maigne et al. (1985), Nguyen Tan et al. (1985). In such systems however, the electron distributions are subject to changes relative to the bulk due to size effect; moreover when interfaces are reactive, stoichiometry of compounds may vary as a function of the thickness of the deposit. So the true solid/solid interfaces are not necessarily analyzed. In any case the whole deposit contributes to the electron spectrum rather than just the interfacial layer so that the electron distribution of the interface cannot be obtained directly.

X-ray emission spectroscopy can be used as a tool for depth profile analysis of the occupied density of states (Szasz and Kojnok, 1985). If the X-ray emission is excited by means of electrons it is possible to vary the thickness contributing to the emission by controlling the penetration of the incident electrons which is known to depend on their kinetic energy. The profile analysis of thicknesses from 10 nm to 4 μm can include an interfacial region. The depth resolution is about 5 nm.

To analyze the distribution of empty states as a function of sample depth a method which records the Auger yield has been proposed (Bedzyk and Materlik, 1985). Auger electrons are produced as the energy of incident photons is varied over a photoabsorption threshold and are registered in an energy dispersive mode. This method is depth sensitive because an electron originating from

close to the surface will be detected with a higher energy than an electron (of the same initial energy) originating from deeper down in the sample; it has proved to be very useful in the study of samples whose stoichiometry varies as a function of depth. Its application to interface studies has been suggested but the resolution is no better than a few hundred Å.

It appears of great interest to have a method able to analyze, with a resolution of one interatomic distance, a given type of atom present in the contact region between two materials. We show hereafter that this can be performed by X-ray emission spectroscopy when induced by electrons of appropriate kinetic energy. Spectra can be obtained from the interface atoms only, quite separately from the rest of the sample. First we recall some basic principles of the X-ray emission process. Then we explain its use for analysis of solid/solid interfaces (Fargues et al., 1985 a).Finally we present typical examples of what we have obtained (Iraqi et al., 1985, Fargues et al., 1985b). Various phenomena can occur at an interface : essentially surface, size, and chemical effects. We discuss each of them in relation to free surfaces, small particles and bulk compounds.

### Principle of X-ray emission

X-ray emission results from the radiative decay of an excited or ionized state with a hole in a core level (figure 1a) noted intermediate
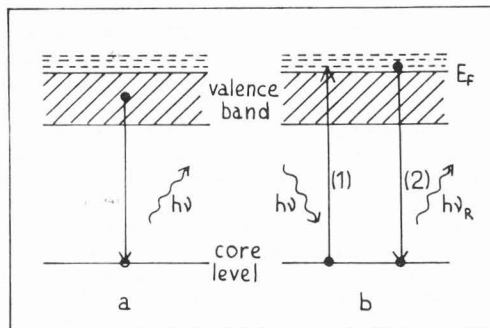


Figure 1 : (a) Schematic representation of X-ray transitions giving rise to an X-ray emission band. (b)(1) photoabsorption process:the incident photon is absorbed and a core electron is excited to an empty level.(2) Resonant X-ray emission (in a small metallic particle for example).

state. Information about the density of valence states can be obtained from emission bands involving transitions from valence electrons towards an inner level. Electric dipole selection rules fix the symmetry of states which take part in transitions to an $nlj$ inner hole. When different types of atoms are present in a sample, their emission spectra are generally sufficiently separated in energy to allow a separate study of each species. Lastly, when an excited intermediate state has a lifetime of the order of or greater than that of the inner hole, in other words when it is strongly localized, a resonant X-ray emission is observable in coincidence with a strong maximum of the photoabsorption spectrum (Bonnelle, 1982) (fi-

gure 1b). This contributes to information on the localization of empty states.

The emission precursor intermediate state is obtained by interaction between the sample atoms in the ground state and ionizing particles. Commonly photons or electrons are used. Because a photon is annihilated during a photoabsorption process, the energy of incident photons has to be, depending on the intermediate state,
- equal to the excitation energy $E^*$
- equal to or higher than the ionization threshold $E_i$ of the studied atoms.During an ionizing collision the electrons may lose all or part of their initial kinetic energy $E_0$ so that $E_0$ has to be equal to or higher than the threshold energy of excitation or ionization processes.

### X-ray emission induced be electrons applied to the study of interfaces

The aim is to study, from an X-ray emission band, the valence states of an element Z present at the interface between one material 1 and a second covering material 2 which does not contain Z. This is made possible by inducing the X-ray emission by electrons with appropriate energy. After a path $x_2$ in material 2 (figure 2) electrons with
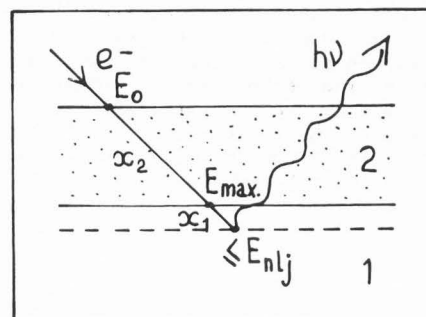


Figure 2: Basic scheme for interface X-ray analysis.

incident kinetic energy $E_0$ will have energies ranging from zero to a maximum value $E_{max}$. Over our experimental conditions, $E_0 < 10keV$ and $x_2 \lesssim 50nm$, the electron energy distribution at the interface is strongly asymmetrical and it depends on the ratio $\mathcal{R} = x_2/\overline{R}_2$, where $\overline{R}_2$ is the maximum range of electrons with initial energy $E_0$ in material 2 (Fitting, 1974, Dejardin-Horgues, 1976). For small values of $\mathcal{R}$, $E_{max}$ is equal to $E_0$; near $E_{max}$, the shape of the energy distribution is narrow and the number of electrons transmitted is high. On the other hand, for $\mathcal{R}$ close to unity , the energy distribution is flattened and broadened, the number of electrons with energy $E_{max}$ is small and $E_{max}$ is lower than $E_0$. The emissive region will be situated just at the interface if the maximum energy $E_{max}$ satisfies the condition:

$$E_{max} \sim E_{nlj} + \varepsilon (1) \qquad (1)$$

where $E_{nlj}$ is the formation energy of the core hole and $\varepsilon(1)$ the average energy loss of electrons with energy $E_{max}$ in a monoatomic thickness of material 1.

Two methods can be used to determine the appropriate value of $E_0$ : a) this $E_0$ can be

deduced from the energy distribution curve of electrons which have traversed material 2. Each energy distribution is characterized by a couple of values of $\mathcal{R}$ and $E_{max}$. Condition (1) fixes $E_{max}$ and thus $\mathcal{R}$. Knowing the experimental parameter $x_2$ one derives from $\mathcal{R}$ the value of $\overline{R_2}$ and then $E_0$ since $\overline{R_2}$ and $E_0$ are related by empirical relations (Young, 1956, Feldman, 1960). It is convenient to have $x_2$ as small as possible so that the electron energy is little dispersed after crossing material 2; however $x_2$ must remain sufficient for material 2 to have bulk properties. This method requires that the energy distributions of electrons in material 2 should be known for a number of energies $E_0$. Its precision is poor except if $x_2$ does not exceed $\sim$ 10 nm, because in this case $E_{max}$ simply equals $E_0$.

b) Another determination of the appropriate value of $E_0$ is obtained from the appearance threshold of an X-ray line, either the considered line of formation energy $E_{nlj}$ or another well resolved line whose formation energy $E_{n'l'j'}$ exceeds $E_{nlj}$ by approximately $\varepsilon$ (1). In practice this condition can be satisfied when the energies $E_{nlj}$ and $E_{n'l'j'}$ differ by the spin orbit coupling. Then, if the value of $E_{max}$ is included between $E_{nl\ j-1}$ and $E_{nlj}$, the emission from nl j-1 is cancelled while that from nlj remains observable. In both cases the appearance threshold $E_0$ is determined from the variation of the line intensities versus the incident energy, i.e. the excitation curves, and the precision depends on the intensity measurements. In the latter case it is possible, from the stopping power in material 1, to determine the range in which the electrons lose an average energy $E_{nl\ j-1} - E_{nlj}$. In figure 3, $x_1$ is
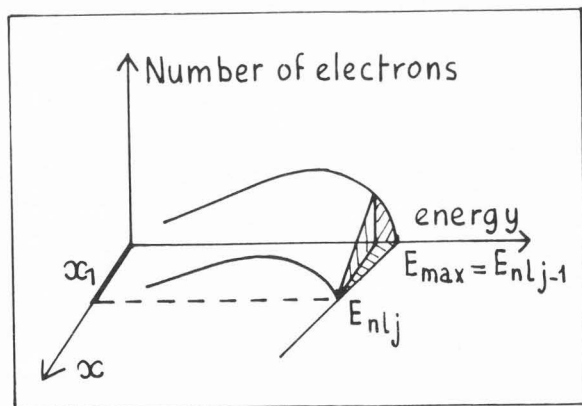


Figure 3 : Electron distribution in the neighbouring of an interface.

the emissive thickness and the shaded area schematically indicates the part of the electron distribution which contributes to create the inner hole in material 1.

Of course the above consideration apply only if the interface is sharp. If we consider the case where material 1 diffuses into material 2, then material 2 contains a small amount of material 1 in the form of small particles or isolated atoms. In such a case the interface is now between bulk material 1 and a mixture of materials 1 and 2 (figure 4). The excitation curves can be
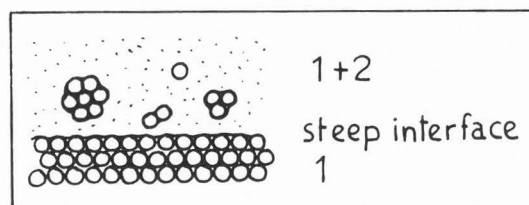


Figure 4 : Model of interface when material 1 diffuses into material 2

experimentally determined as indicated previously. If $E_0$ is the value chosen from these curves the ratio $E_{max}/E_0 \simeq [E_{nlj} + \varepsilon(1)]/E_0$ characterizes one of the energy distribution curves of electrons to which is associated a value of $\mathcal{R}$. Knowing $E_0$ and thus $\overline{R_2}$, it is now possible to derive from $\mathcal{R}$ a value of $x_2$ which we will note $x_2(\mathcal{R})$. This value has to be compared to the experimental $x_2$ measured during the sample preparation. In our model $x_2$ and $x_2(\mathcal{R})$ are related by :

$$x_2(\mathcal{R})\rho_2 = x_2[\alpha\rho_1 + (1-\alpha)\rho_2] \qquad (2)$$

where $\alpha$ is the proportion in weight of material 1 which may be in the upper layer and $\rho_1$, $\rho_2$ are the specific gravities of materials 1 and 2. If $x_2(\mathcal{R}) = x_2$, $\alpha$ is zero and the interface can be considered as steep. On the contrary if $x_2(\mathcal{R})$ differs from $x_2$ the interface is diffuse and relation (2) can be used to give a rough estimate of $\alpha$.

## Examples of solid/solid interface spectra

In order to test our method we have chosen as material 1 an element whose spectrum is well known; nickel is a good candidate owing to the numerous data we have obtained on the effects of chemical bonding and particle size on its spectra. (Bonnelle et al.,(1978), Fargues et al.(1981),Vergand et al.(1981), Vergand et al.(1983),Fargues et al. (1984)). We present hereafter interfaces of bulk nickel and small nickel particles with either an insulator ($MgF_2$) or a good metal (Al). Finally we report on the interface with a porous amorphous oxide : SiO.

The samples are obtained by successive vacuum depositions of the materials 2,1 and 2 on the anode of the X-ray tube at room temperature and characterized as described by Vergand et al.(1983). Ni L$\alpha$ (3d-2$p_{3/2}$) emission is studied: its threshold energy is $E_{2p3/2} \sim$ 853 eV. The appropriate value of $E_0$ is determined experimentally as just less than the appearance threshold of the L$\beta$ emission (3d-2$p_{1/2}$); we show an example of excitation curves in figure 5. The $2p_{1/2}$ threshold energy is $\sim$ 870 eV; thus the $2p_{1/2}$-$2p_{3/2}$ separation is $\sim$ 17 eV; the stopping power of nickel for electrons in the range 870-853 eV being 6 eV. $\mathring{A}^{-1}$ (Ashley et al. (1976)), the emissive thickness is expected to be around 3 $\mathring{A}$ i.e. approximately one interatomic distance.

Let us remark that $E_{max}$ being less than $E\ 2p_{1/2}$ for all interface spectra, the $L_{II}$-$L_{III}\ M_{IV,V}$ satellite will always be absent on all these spectra.
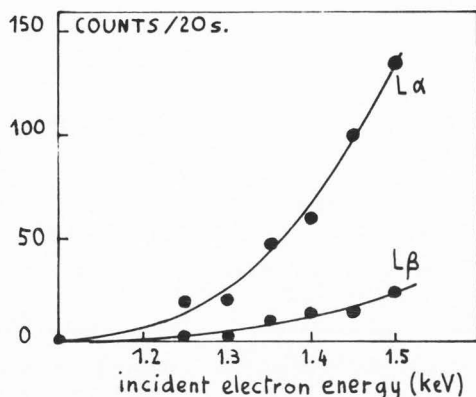
Figure 5 : Excitation curves for small nickel particles/Al interface.



Figure 7 : Ni $L\alpha$ emission : (a) small nickel particles/MgF$_2$ interface with $x_2 = 50 \pm 10$ nm, $E_0 = 1.3$ keV. (b) whole particle spectrum.
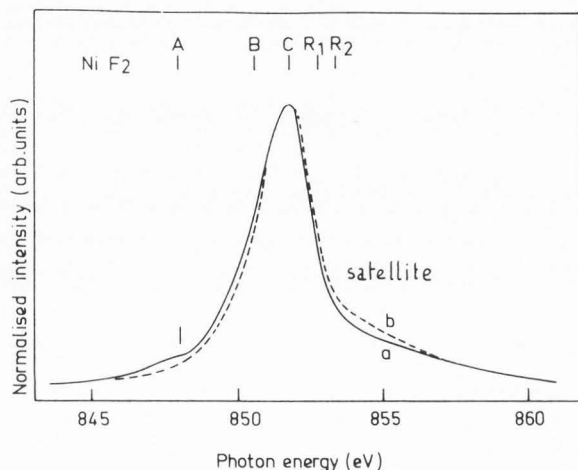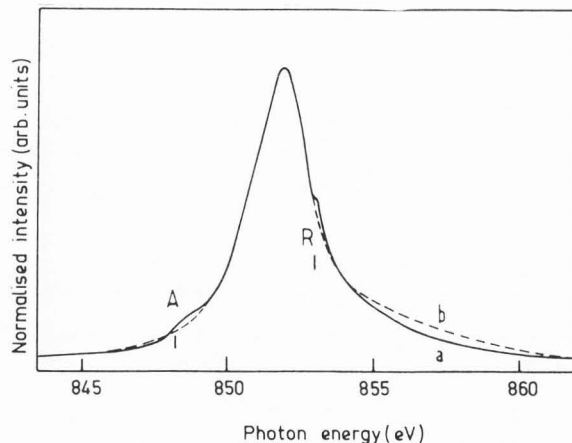


Figure 6 : Ni $L\alpha$ emission : (a) bulk Ni/MgF$_2$ interface with $x_2 = 37 \pm 7$ nm, $E_0 = 1.3$ keV; (b) bulk nickel. Bars indicate the positions of the features characteristic of NiF$_2$.

## Bulk nickel/MgF$_2$

The $L\alpha$ emission of bulk nickel/MgF$_2$ interface is presented in figure 6a and compared to the pure bulk nickel (figure 6b). The $L\alpha$ emission of NiF$_2$ compound shows several features whose positions are indicated as bars in the figure. While the bulk nickel spectrum does not present any feature, that of interface shows clearly a feature noted A. This low energy feature of the $L\alpha$ emission indicates the mixing of Ni 3d character states with F 2p states and characterizes the existence of an orbital with hybridized p – d character partly lying on the nickel site. Features of the same type are observed in the spectra of various ionic compounds and are generally called interatomic transitions. On the other hand the splitting of the d band due to the octahedral crystal field of fluorine ions, which gives rise to the B shoulder and the main maximum C in stoichiometric NiF$_2$, is not observed at the interface. Thus no tridimensional

NiF$_2$ compound is observable. The mixing of Ni and F states occurs only for nearest neighbour atoms and the interface can be considered as steep. Resonances R$_1$ and R$_2$ do not appear because the vicinity of the extended empty states of bulk nickel is opposed to the localization at the interface.

## Small nickel particles/MgF$_2$

In figure 7, curve a, we show the $L\alpha$ emission of the interface between small particles (mean size 2.2 nm) and MgF$_2$; $L\alpha$ of the whole particles is drawn for comparison, curve b, (Iraqi et al. (1985)). It must be emphasized that these two curves are different, proving on an experimental basis our method has a resolution much better than 2 nm. The main part of the emission is contracted relative to the bulk and a resonant emission R is present for the interface attesting to an increase of the localization of the occupied as well as empty states when one goes from bulk metal to small particles and then to the surface of the small particles. This increasing localization is related to the decrease of the mean coordination number. It is like a surface effect and involves a dehybridization of the s – d nickel states. On the other hand, as expected since nickel atoms are close to fluorine atoms, transition A is observed.

## Bulk nickel and small nickel particles/Al

Let us consider now the interface between nickel and a good metal with extended s – p states, like aluminium. In figure 8 we have reported the bulk nickel interface (curve a) and the small particle (1.7 nm) interface (curve b) $L\alpha$ emissions both compared to the bulk nickel $L\alpha$ emission (dotted curves). At each interface two processes occur which lead to opposite results : i- dehybridization of the s – d states of nickel due to surface effect which lead to a decrease of the d band width; ii- hybridization between Ni d states and valence Al s – p states which leads to an increase of the d band whidth. One can clearly see the two processes cancel rather well at the bulk nickel interface :
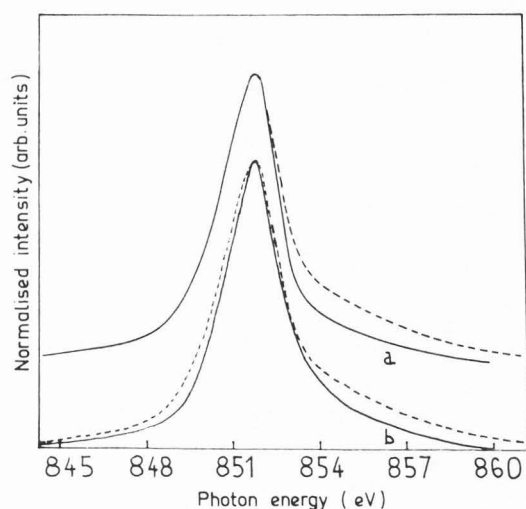
Figure 8 : Ni Lα emission. Full lines : (a) bulk nickel/Al interface with $x_2$ = 44 ± 8 nm, $E_0$ = 1.1 keV. (b) small nickel particles/Al interface with $x_2$ = 42 ± 8 nm, $E_0$ = 1.1 keV. Dotted lines : bulk nickel.



Figure 9: Ni Lα emission of Ni/SiO interface with $x_2$ = 37 ± 7 nm, $E_0$ = 1.75 keV.

in fact there is no difference in the main part of the interface emission relative to the bulk metal. The only difference lies in the satellite range as we have seen above. When nickel atoms belong to a small particle the dehybridization of the s − d states due to the surface effect is stronger than in bulk nickel. As a consequence this effect is stronger than the hybridisation Ni d − Al s − p due to Ni −Al vicinity. Indeed we observe a clear contraction of the emission band of the small particle interface.

It must be underlined that for Ni/MgF$_2$ and Ni/Al interfaces the coefficient α of relation (2) was found to be zero; it confirms the interfaces are steep in agreement with the above results.

Nickel/SiO

Silicon monoxide is known to be a porous material, so it is expected to form a diffuse interface with nickel. The Ni Lα emission from a bulk nickel film covered with SiO was performed with $E_0$ a little lower than the experimental threshold of Lβ emission. From relation (2) we found α ∼ 0,2 confirming the diffuse character of this interface. The interface spectrum we obtained is reported in figure 9. There, we recognize two kinds of features : i- structures noted a to e which are typical of small particles whose size is less than one hundred atoms; ii- a structure noted t and a faint shoulder c' which are respectively an interatomic transition and the main maximum of the NiO emission band, both characteristic of chemical interaction between Ni and Si and O. The latter features are not observed in the spectrum of small Ni particles (mean size 1.5 nm) embedded in SiO; thus the chemical interactions Ni-O and Ni-Si only concern nearest neighbour atoms and there is not any tridimensional silicide or oxide formed at room temperature. Nevertheless approximately 20% of nickel are present in the upper layer of SiO and contribute to the emission spectrum. This spectrum is the sum of
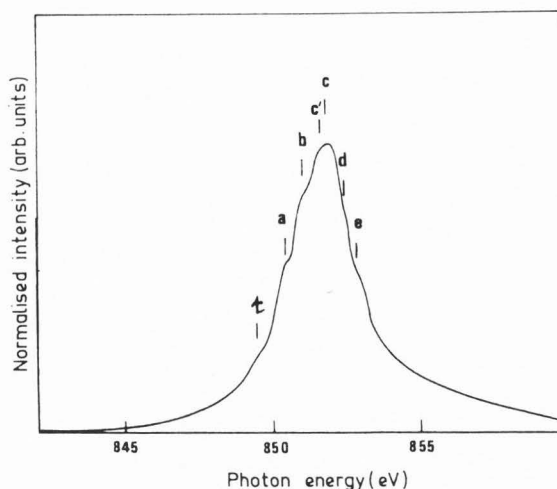
the contributions due to nickel atoms and aggregates included in SiO and of a quasi-monoatomic layer at the top of the bulk nickel layer.

## Conclusion

The few examples reported here show X-ray emission spectroscopy gives useful information on the nature of the interfaces, both electronic and structural ones, with a resolution around one interatomic distance. By means of this method it has been possible to evidence bonding effects, localization and dehybridization of valence states due to interactions between atoms in contact. On the other hand it was shown whether the interface was steep or diffuse and a rough estimate of the diffused amount was given.

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## Discussion with Reviewers

S.Hofmann : As seen from Fig. 2, the energy $E_{max}$ depends critically on the path length $x_2$. Therefore, any roughness of the surface of material 2 should blur the apparent interface width and hence the depth resolution of the method, and likewise the distinction between steep or diffuse interfaces.

Author : Two kinds of roughnesses may be considered at the surface of the anodes where the films are deposited : i- microscopic defects : we assume that, they are more or less smoothed by the first deposition of material 2; ii- long range undulations : we assume that they are repeated through the successive film depositions. So we think that the path length $x_2$ is quite constant and the actual emissive thickness is of order of the calculated one.

S. Hofmann: What the author calls "depth resolution" is only defined on a theoretical basis depending on the specific energy loss of electrons in a certain material. If the author claims that the resolution is much better than 2nm, this is only an indirect argument deduced from the mean size of the Ni particles (2.2nm). Furthermore, obtained signal to noise ratios should be given for the spectra to get a feeling for the significance of the small differences in the recorded spectra (Figs. 6-8). Lateral beam dimensions and roughness effects should be discussed.

C.E. Bryson: The data should be accompanied by more detail about the experience: signal to noise ratio, lateral beam dimension, data acquisition.

Author : A bent crystal vacuum spectrometer (principle of Johann) is used. The X-ray spectra are recorded in a 1' step - to - step fashion along the focalization circle through a 150 μm slit. A beryl crystal of radius 500 mm, provides an accuracy of 0.1 eV along the photon energy scale in the Ni L α range. The signal to noise ratio

decreases with decreasing the emissive thickness.
It can be 20,000 for bulk nickel(8 scans, coun-
ting time per point 20 s, electron beam in the
X-ray tube 30 mA) leading to an accuracy on re-
lative intensity of 0.2%. The signal to noise
ratio is only ~ 15 for an abrupt interface
(Ni/Al or Ni/MgF$_2$); by adding twenty five scans
we obtain an accuracy on the normalized intensi-
ty about 2%.

C.E.Bryson : Depending on the thickness of the
overlayer, one would expect the surface to char-
ge when the overlayer is an insulator. How were
the resulting potentials dealt with?
Author : It is necessary to take into account the
potential resulting from the charge of the sam-
ple if the appropriate value of E$_0$, that forces
condition (1) to be fulfiled, is determined from
the energy distribution curves of electrons.
This potential, when it exists, will shift by a
few eV the energy scale of the experimental ex-
citation curves and in particular the appearance
threshold of the studied emission lines. When
the appropriate value of E$_0$ is determined from
this appearance threshold itself no error is
introduced. The examples presented in this paper
correspond to the latter case.