



HAL
open science

SURFACE EXAFS AND XANES STUDIES OF S/Ni (110) AND S/Ni (111)

T. Ohta, Y. Kitajima, P. Stefan, M. Shek Stefan, N. Kosugi, H. Kuroda

► **To cite this version:**

T. Ohta, Y. Kitajima, P. Stefan, M. Shek Stefan, N. Kosugi, et al.. SURFACE EXAFS AND XANES STUDIES OF S/Ni (110) AND S/Ni (111). *Journal de Physique Colloques*, 1986, 47 (C8), pp.C8-503-C8-508. 10.1051/jphyscol:1986894 . jpa-00226225

HAL Id: jpa-00226225

<https://hal.science/jpa-00226225>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

SURFACE SEXAFS AND XANES STUDIES OF S/Ni(110) AND S/Ni (111)

T. OHTA, Y. KITAJIMA*, P.M. STEFAN**, M.L. SHEK STEFAN***, N. KOSUGI* and H. KURODA*

Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Ibaraki 305, Japan

**Department of Chemistry, Faculty of Science, the University of Tokyo, Hongo, Tokyo 113, Japan*

***NSLS, Brookhaven National Laboratory, Upton, Long Island, NY 11973, U.S.A.*

****Department of Physics, Brookhaven National Laboratory, Upton, Long Island, NY 11973, U.S.A.*

ABSTRACT

S K-edge SEXAFS were measured on $c(2 \times 2)S/Ni(110)$ and $S/Ni(111)$ by monitoring the S KLL Auger intensity as a function of photon energy and polarization direction. Analysis of the data from $c(2 \times 2)S/Ni(110)$ gave results that a sulfur atom is located on a hollow site with $R(S\text{-top layer Ni})$ of $(2.31 \pm 0.02) \text{ \AA}$ and $R(S\text{-bottom Ni})$ of $(2.19 \pm 0.03) \text{ \AA}$. These results are in close agreement with the recent analysis of LEED. From the preliminary SEXAFS work on $p(2 \times 2)S/Ni(111)$, S-nearest neighbor Ni bond distance was determined to be $2.20 \pm 0.04 \text{ \AA}$.

INTRODUCTION

Now, SEXAFS has been proved to be a powerful technique for surface structure analysis. However, this method has been applied to only less than 30 systems, since 1978, when the pioneering works were performed by P. Citrin et al.[1] and J. Stöhr et al.[2] at SSRL. This is mainly due to the limited experimental facilities available in the world. Recently, several groups in Daresbury[3] and also BESSY[4] reported the SEXAFS works. Here we present the first SEXAFS experiment carried out at the Photon Factory.

$c(2 \times 2)S/Ni(100)$ was studied extensively by S. Brennan et al.[5] using polarization dependent SEXAFS, but sulfur on other two faces have not been studied with SEXAFS yet. Recently, Baudoing et al.[6] carried out the precise LEED analysis of $c(2 \times 2)S/Ni(110)$ and found the drastic relaxation of the Ni top and second layers. The LEED is rather sensitive to the interplanar spacing, while the SEXAFS gives the local bond distance in a theory independent fashion. Accordingly, it is worthwhile to investigate the same system with the SEXAFS method. In this report, S on Ni(110) and Ni(111) were studied using the polarization dependent SEXAFS.

EXPERIMENTAL

High purity (5N) single crystals with two faces, (110) and (111) were purchased from Metal Crystals and Oxides Ltd. in U.K.. Disk-shaped ($2 \text{ mm}^t \times 10 \text{ mm } \Phi$) crystals were polished down mechanically to $1 \mu\text{m}$ with a diamond paste and then electro-polished. Each sample was cleaned in a UHV chamber by the successive treatment of Ar^+ sputtering and annealing ($\sim 800 \text{ }^\circ\text{C}$). Surface cleanness and crystal perfectness were monitored with AES (Auger Electron Spectroscopy) and LEED. After 5 to 10 cycles of cleaning, we could obtain clean Ni crystal surfaces, on which S and C were nondetectable with AES.

Sulfur overlayer was produced by dosing H_2S on each clean crystal. About 2 Langmuir of H_2S ($10^{-7} \text{ torr} \times 20 \text{ sec}$) was dosed on the Ni(110) crystal, heated at about $200 \text{ }^\circ\text{C}$. Bright $c(2 \times 2)$ LEED pattern was observed and this surface structure was stable at least for 24 hours under the base pressure lower than 10^{-10} torr .

For the case of Ni(111), the dosage of 1 L H_2S on the sample at room temperature yielded $p(2 \times 2)$ pattern, while more than 3 L dosage yielded very complicated ($5\sqrt{3} \times 2$) pattern. These surface structures were comparatively unstable and their LEED spots became dim after 6 hours.

Surface EXAFS experiments were performed using synchrotron radiation from the soft X-ray double crystal monochromator at the Photon Factory[7].

By use of a set of InSb(111) crystal pair, the photon flux of $\sim 5 \times 10^{10}$ photons/sec is available in the 1650~3800 eV energy range with 1.5 eV resolution. The SEXAFS signal was obtained by monitoring the S KLL Auger electron yield, whose energy is $\sim 2100 \text{ eV}$. Spectra were recorded using a cylindrical mirror analyser (CMA) in the nonretarding mode, and were flux normalized by a monitor consisting of a Cu grid and a spiraltron electron multiplier. It took about 1.5 hours to obtain each EXAFS spectrum in the range 2400-2900 eV, whose upper energy is limited by the appearance of the Ni 2p photoelectrons in the CMA window.

Ni_3S_2 was chosen as a model compound, in which the nearest neighbor bond length of S-Ni is $2.28 \pm 0.01 \text{ \AA}$, and the coordination number is 6[8]. Total electron yield spectrum of a sintered disk of Ni_3S_2 was measured in the same energy range as that for SEXAFS spectra of above-described systems.

In the case of S on Ni(110), there are two angular dependences: (i) on the polar angle θ between the \vec{E} vector and the surface normal \vec{n} and (ii) on the azimuthal angle ϕ in the surface plane. Thus, we measured two polar-angle dependent SEXAFS spectra; one for \vec{E} parallel to the [100] ($\phi = 0^\circ$) and the other for \vec{E} parallel to [110] ($\phi = 90^\circ$). On the other hand, there are no azimuthal angular dependence of SEXAFS for S/Ni(111) and we measured polarization dependent SEXAFS spectra for one azimuthal angle.

RESULTS AND DISCUSSION

(a) $c(2 \times 2)S/Ni(110)$

Figure 1 shows the raw S K-edge SEXAFS spectra of $c(2 \times 2)S/Ni(110)$ at photon incident angles θ of 90° , 45° , and 10° at $\phi = 0^\circ$. The oscillations and their polarization dependency are visible with good signal to noise ratio. The background was subtracted from each spectrum assuming that it follows the sulfur atomic absorption above the edge. The EXAFS signal $\chi(k)$ was normalized to the edge height, which was determined by extrapolating the atomic absorption line to the edge. Fourier transform of $\chi(k) \times k^2$ (Fig. 2) shows a strong peak around 2 \AA , which can be assigned to S-nearest neighbor Ni, although its distance is apparently shorter due to the phase shift. After filtering, the strong peak in the R-space was Fourier transformed back into k-space, which gave the amplitude of the nearest neighbor bond. By comparing the amplitude function with that from the model compound, Ni_3S_2 , we could obtain the effective coordination number N^* at each angle. As shown in Fig. 3, there are four kinds of possible adsorption sites for S on Ni(110). The effective coordination number N^* was calculated for each possible adsorption site, assuming the nearest S-Ni bond length to be 2.31 \AA .

Calculated and experimental N^* s are compared in Table 1. It is possible to determine the adsorption site uniquely as a hollow site from the data for two azimuthal angles, $\phi = 0^\circ$ and $\phi = 90^\circ$.

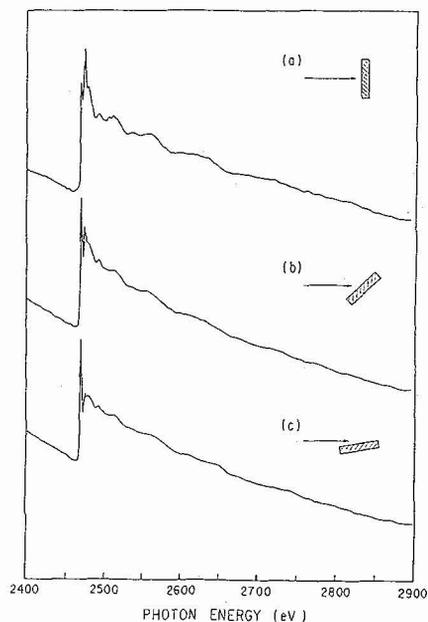


Fig.1 S K-edge SEXAFS spectra of $c(2 \times 2)S/Ni(110)$ at $\phi = 0^\circ$, with three polar angles, (a) $\theta = 90^\circ$, (b) $\theta = 45^\circ$, (c) $\theta = 10^\circ$.

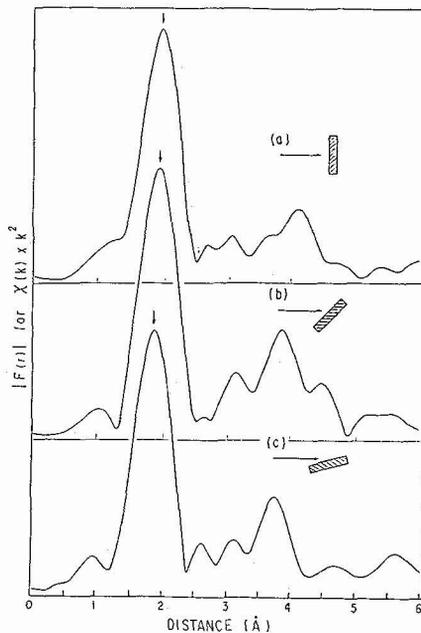


Fig.2 Fourier transform of $\chi(k) \times k^2$ for SEXAFS spectra in Fig.1

Back to the Fourier transformed spectra (Fig. 2), it should be noted that the peak position is shifted to the shorter distance by changing the angle θ from normal to grazing incidence. This result indicates that the peak contains two components; one from the top layer four nickel

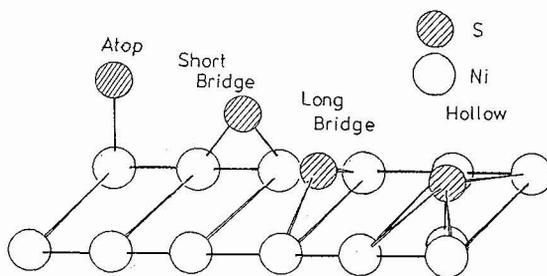


Fig. 3 Possible adsorption site of S on Ni(110)

atoms and another from the bottom nickel atom. At the normal incidence, there is no contribution to EXAFS from the bottom nickel atom. Thus, we can easily determine the bond length between S and four top layer Ni atoms, R_{top} , as $2.31 \pm 0.02 \text{ \AA}$. Next, we determined the bond length of S-bottom Ni, R_{bottom} , through the least square fit, where R_{top} and σ_{top} and N^*_{top}/N^*_{bottom} were fixed, and R_{bottom} , σ_{bottom} , and N^*_{bottom} were parametrized. The value obtained was $2.19 \pm 0.02 \text{ \AA}$. By using the determined bond lengths, we can get the inter-spacing between the top layer and the second layer, which is $1.37 \pm 0.02 \text{ \AA}$. This is longer than the bulk interlayer spacing, 1.246 \AA by $(10 \pm 2)\%$. It indicates that the strong bond between the S atom and the bottom Ni (second layer) pushes the top layer Ni upwards. These results are in close agreement with those by Baudoing et al.[6] who analysed the LEED data, taking the multilayer relaxation into account.

Table 1 Comparison of Experimental and Calculated N^*

Curve Fitting of Obsd. Spectra			Calcd. Coordination Number N^*					
Polorization	R	N^*	Atop	Short	Long	Hollow	Hollow**	
ϕ θ	\AA			Bridge	Bridge			
0°	90°	2.31	5.83	0	0	3.62	6.98	6.98
	45°	2.28	4.58	1.5	2.10	3.00	4.25	5.75
	10°	2.22	3.69	2.91	4.07	2.42	1.69	4.60
$N^*(90^\circ)/N^*(45^\circ)$			1.27	0	0	1.21	1.64	1.21
$N^*(10^\circ)/N^*(45^\circ)$			0.81	1.94	1.94	0.81	0.40	0.80
90°	90°	2.31	2.74	0	1.80	0	3.49	3.49
	45°	2.26	2.55	1.5	3.00	1.19	2.51	4.01
	10°	2.24	3.45	2.91	4.12	2.31	1.59	4.50
$N^*(90^\circ)/N^*(45^\circ)$			1.07	0	0.60	0	1.39	0.87
$N^*(10^\circ)/N^*(45^\circ)$			1.35	1.94	1.37	1.94	0.63	1.12

Hollow**; results including the bottom Ni atom,

S K edge XANES spectra of $c(2 \times 2)S/Ni(110)$ are shown in Fig. 4, which indicates distinct polarization dependence of the spectra. Here, we denote the coordinate of the $S/Ni(110)$ system as the x axis along $\langle 100 \rangle$, y axis along $\langle 110 \rangle$ and z axis along the surface normal. The XANES spectrum at $\phi = 0^\circ$ and $\theta = 90^\circ$ comes from x-polarized transitions, and that at $\phi = 90^\circ$ and $\theta = 90^\circ$ from y-polarized transitions, while the spectrum at grazing incidence is dominated by z-polarized transitions. According to the preliminary ab initio SCF-MO calculation for the Ni_5S cluster, there is a strong bond between the S atom and the bottom Ni atom, and 4 top layer Ni atoms are rather nonbonding.

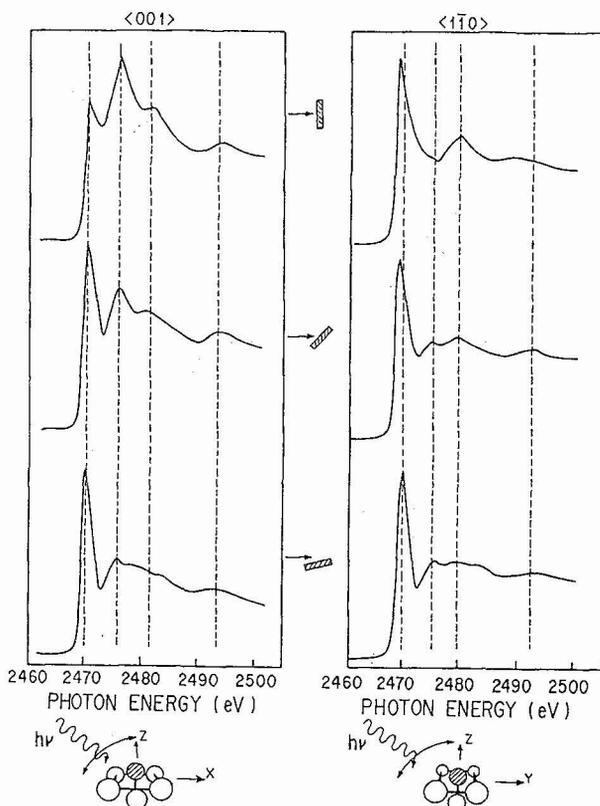


Fig. 4 S K XANES of $c(2 \times 2)S/Ni(110)$

Accordingly, the first peak of z-polarized spectrum can be assigned to be the transition to the antibonding $(S3p_\sigma - Ni4s_\sigma)^*$ orbital. x- and y-polarized spectra show prominent peaks at the nearly same energy. They are tentatively assigned as the transitions to Rydberg($4P$) type orbitals, where $4P_y$ is slightly lower than $4p_x$, due to the less repulsive force from the surrounding Ni atoms. There are several distinct peaks in the higher energy region, polarized either to x or y. They are possibly due to the shape resonance type transitions. Further detailed calculations are now in progress.

(b) $S/Ni(111)$

The surface structure of this system has been studied little. Rather old LEED analysis by Demuth et al.[9] showed that a S atom is located at three-fold hollow site and the nearest S-Ni bond distance is $2.02 \pm 0.06 \text{ \AA}$. But, it is worth noting that they used only three beam spectra. We performed the SEXAFS measurement both for $p(2 \times 2)$ and $(5\sqrt{3} \times 2)S/Ni(111)$. $\chi(k) \times k^2$ and Fourier transform of the spectra is shown in Fig. 5. By the phase shift correction, the nearest S-Ni bond

distance was determined to be $2.20 \pm 0.04 \text{ \AA}$ for $p(2 \times 2)$ and $2.18 \pm 0.03 \text{ \AA}$ for $(5\sqrt{3} \times 2)S/Ni(111)$. These values are more probable than that determined with LEED. There are three possible adsorption sites; atop, bridge and hollow site. Since the S K XANES spectra for $p(2 \times 2)S/Ni(111)$ do not show any distinct polarization dependence, we can exclude the atop site. Further detailed experiment is necessary to determine the adsorption site in conclusive way.

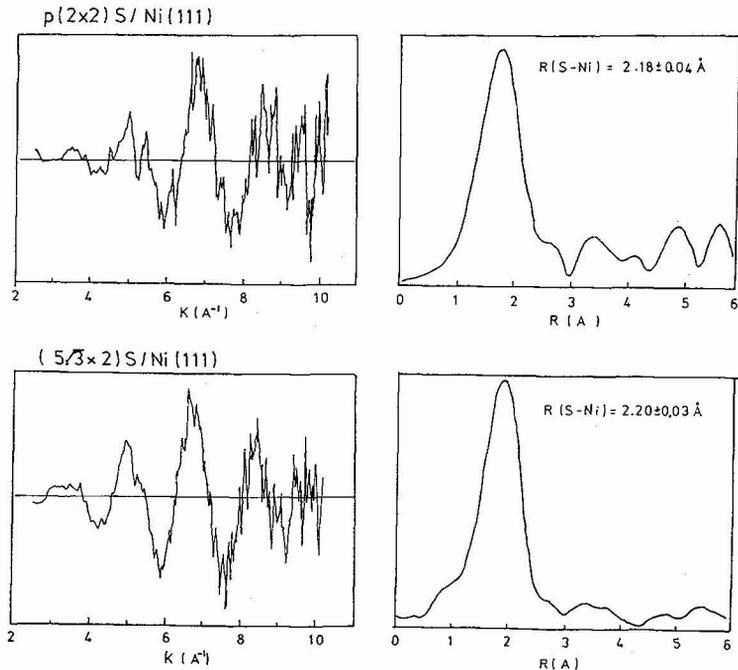


Fig. 5 $\chi(k) \times k^2$ and Fourier transform of SEXAFS spectra from $p(2 \times 2)S/Ni(111)$ and $(5\sqrt{3} \times 2)S/Ni(111)$

REFERENCES

- (1) P. H. Citrin, P. Eisenberger, and R. C. Hewitt: Phys. Rev. Lett. 41 (1978) 309.
- (2) J. Stöhr, D. Denley, and P. Perfetti: Phys. Rev. B18 (1978) 4132.
- (3) G. M. Lambie, R. S. Brooks, S. Ferrer, D. A. King and D. Norman: Preprint of Daresbury Lab. Jan. (1986).
- (4) U. Döbler, K. Baberschke, J. Haase, and A. Puschmann: Surf. Sci. 152/153 (1985) 569.
- (5) S. Brennan, J. Stöhr and R. Jaeger: Phys. Rev. E24 (1981) 4871.
- (6) R. Baudoing, Y. Gauthier, and Y. Joly: J. Phys. C18 (1985) 4061.
- (7) T. Ohta, P. M. Stefan, M. Nomura, and H. Sekiyama: Nucl. Inst. and Methods. A246 (1986) 373.
- (8) R. W. G. Wyckoff: "Crystal Structures" Vol. 2, p.24 (Wiley, New York, 1964).
- (9) J. E. Demuth, D. W. Jepsen, and P. M. Marcus: Phys. Rev. Lett. 32 (1974) 1182.