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EELFS as a new tool of local structural characterization of solid surfaces

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A new apparatus to obtain information on local structures and chemical states of solid surfaces has been constructed, with which we measure electron energy-loss fine structures (EELFS), excited by electrons of a few keV incident at a grazing angle. We describe results about O/Ni(100) and O/W(100) systems, where we extensively take advantage of anisotropy in regard to momentum transfer of the probe electron and high surface sensitivity of this technique.

Keywords: EELFS; ELNES; local surface structure; momentum transfer; O/Ni(100); O/W(100)

1. Introduction

EELFS (electron energy-loss fine structure) was initially observed in an energy spectrum of electron transmission microscopy at a high energy [1]. EELFS may be classified into EXELFS (extended energy-loss fine structure) and ELNES (energy-loss near-edge structure) in a similar manner to EXAFS and XANES in XAFS, while the terminology has been unsettled yet. Being scattered by incident electrons, excited electrons propagate in a solid and are reflected by the nearest-neighbor atoms. The interference between this outgoing electron and the reflected one, as in the case of XAFS, will induce changes in the yield of electron excitation in mother atoms. When scattered electrons are counted as a function of their kinetic energies, one can observe an oscillatory spectrum following to a core-electron energy-loss edge (EXELFS), just like EXAFS. Therefore, the Fourier transform for such an electron energy-loss fine structure is able to give a local inter-atomic distance in a solid. On the other hand, studies on energy-loss near-edge region

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(ELNES) have often been performed as finger printing to identify the chemical states of specified atoms surrounded by other species [2].

Studies on EXAFS in an X-ray adsorption spectrum extensively have been developed to obtain structural information on condensed matters in detail, since a strong light source such as a storage ring has been available. However, on the other hand, such investigations necessarily need to be carried out only at large-scale research centers.

EELFS, instead, is easy to be measured in an individual laboratory, as it can be operated with electron beams of a few keV. Therefore, even in a small home laboratory, one can perform an equivalent measurement to XAFS by means of EELFS. Such a research circumstance should be desirable for promoting studies on catalysis, since information on local atomic configurations and chemical states on a surface is one of the basic data to analyze catalytic reactions. So far, to develop a new technique mentioned above, constant efforts have been made for several years [3–5]. Tyliszczak and his colleague have also carried out their experimental works for the same purpose [6–8].

This report describes that to obtain local structural information at a solid surface, a proper experimental set-up for EELFS has been examined from the theoretical point of view, then apparatus have been constructed to realize the required arrangement. The performance of the apparatus has been checked and some results have also been described.

2. Theoretical background

Since a pioneering work was published in 1971 [9], theory of XAFS has been improved using more precise expressions for approximate formulations. On the other hand, an attempt has recently been made to establish sophisticated many-body EELFS theories including all loss effects in a bulk [10,11]. Guiding principles for conducting experiments, however, can be indicated with simpler theories based on the Bethe approximation [4]. The interaction between photon and electron is expressed in the electric dipole transition mode [12] and the cross section σ(X-ray) is proportional to

$$|\langle\phi_\mathrm{f}|\boldsymbol{\varepsilon}\cdot\boldsymbol{r}|\phi_\mathrm{i}\rangle|^2 . \tag{1}$$

Here, ϕ_i, ϕ_f are the wave functions of electrons before and after the interaction respectively. $\boldsymbol{\varepsilon}$ is the electric field vector of photon and $\boldsymbol{r}$ is the position of electrons concerned.

On the other hand, the cross section of electron–electron interaction σ(electron) is proportional to

$$|\langle\phi_\mathrm{f}|\exp(-\mathrm{i}\Delta\boldsymbol{p}\cdot\boldsymbol{r})|\phi_\mathrm{i}\rangle|^2/|\Delta\boldsymbol{p}|^4 , \tag{2}$$

where $\Delta\boldsymbol{p}$ is a momentum transfer of the incident electron when being scattered.

Then, only under the condition $\Delta \boldsymbol{p} \cdot \boldsymbol{r} \ll 1$, σ(electron) is reduced approximately to

$$|\langle \phi_f| - i\Delta \boldsymbol{p} \cdot \boldsymbol{r} |\phi_i\rangle|^2 / |\Delta \boldsymbol{p}|^4, \tag{3}$$

which is consistent with the σ(X-ray) except for the overall factor. Here, $\Delta \boldsymbol{p}$ in EELFS is understood to play a role of ε in EXAFS.

This condition $\Delta \boldsymbol{p} \cdot \boldsymbol{r} \ll 1$ is essential for EELFS to give rise to equivalent fine structures to XAFS. Bearing this theoretical consideration in mind, the experiment has been arranged so as to irradiate electrons on a sample at a grazing angle and to detect forward-scattering electrons.

This set-up follows several desirable features. First, it will be more surface-sensitive because of grazing incidence condition. Second, as the mathematical expression for cross section is inversely proportional to $|\Delta \boldsymbol{p}|^4$, detection of forward-scattering electrons is expected to be of more advantage.

In the practical sense, the thickness of a sample does not need to be reduced so as to permit transmission of electron through it. In addition, low-Z elements such as carbon, nitrogen, and oxygen can be detected in a higher sensitivity than the XAFS experiment.

Recently, a number of studies on surface structure of a solid have extensively been carried out, using conventional electron spectrometers for AES [13]. These works seem to have shown reasonable experimental results. On the basis of the above theoretical notice, however, radial distributions obtained by applying the Fourier transform to such data, are hardly assured to represent substantial interatomic distances, unless being corrected for possible other kinds of transition than that of dipole type.

Then, an attempt has been made to interpret the energy-loss fine structure observed by detecting back-scattering electrons from a theoretical view point. Calculations for σ(electron), including additional elastic scattering of a probe electron have been carried out. The results show that a different kind of oscillation from EELFS should overlap with EELFS structure and it could be difficult to be removed [5,14].

The theoretical analyses for the amplitude and phase of an oscillating term in the expression of the cross section of EELFS by using the newly developed theory have also been performed. It again has approved that the detection scheme of forward-scattering electrons has some desirable features in k (wave number) dependence, which will be reported in detail elsewhere [14,15].

3. Experimental

An apparatus that satisfies the theoretical requirement, has been constructed, as shown in fig. 1. More details were described in a previous paper [16]. Another apparatus of more improved facilities has been developed [17]. It is provided with a

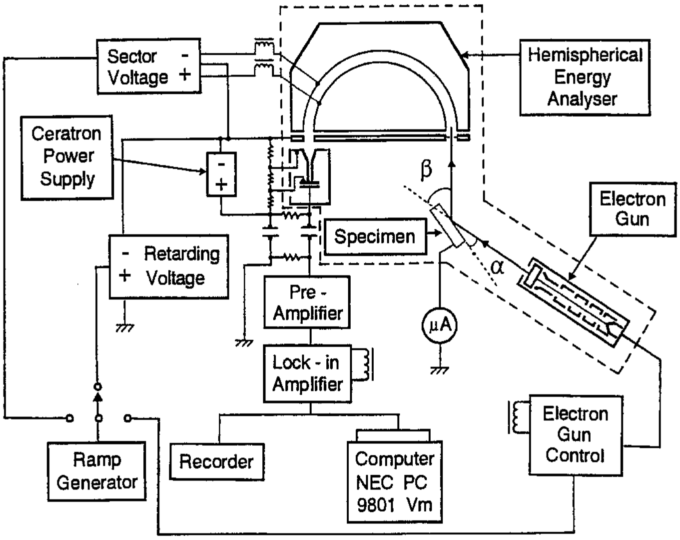

Fig. 1. Block diagram of EELFS apparatus for detecting forward-scattering electrons at a grazing angle [16].

hemispherical analyzer of 150 mm in a mean orbital radius and with an electron gun that can be direction adjustable, being mounted with a flexible bellows. The base pressure of the vacuum chamber is 3×10^{-8} Pa. The electron detection is performed by counting technique. The detection system is composed of five channeltrons, each of which has the maximum counting rate of about 10^6 cps.

Specimens are (100) oriented single crystalline disks of Ni and W, both of which are commercial products (Ni: Monocrystal Ltd., USA; W: Metal Crystal & Oxides Ltd., UK). Surfaces were polished mechanically and then electrolytically to final mirror finish. In addition, a single crystal of NiO was cleaved in parallel to a ⟨100⟩ direction and its surface was examined to compare with results for an oxygen covered Ni(100) surface. Spectroscopically pure oxygen was admitted in the vacuum system through a variable leak valve.

All measured spectra for a W(100) surface were obtained by a lock-in-amplifier and stored in a computer memory. After removing background and integrating thus resulted data, the Fourier transformation was applied to thus obtained spectra with the same personal computer. LEED observations were also carried out to find information on superstructures induced by oxygen adsorption on Ni(100).

4. Results and discussion

4.1. OXYGEN ON Ni(100)

As a performance test of the improved apparatus, a cleaved NiO(100) surface has been used as a specimen, since the data on surface-XANES for this kind of surface are available [17]. Fig. 2. shows the ELNES for oxygen K-edge obtained in the present work, together with the above-mentioned XANES spectrum. Both spectra can be regarded to be in good agreement.

After cleaning a Ni(100) surface, oxygen was admitted in the chamber. It resulted in the formation of three different surface-structures, p(2 × 2), c(2 × 2), and NiO layer at a room temperature, dependent on oxygen exposure. The final one, which is here indicated as NiO/Ni(100), can be visible with 3000 L and gentle annealing followed. ELNES spectra for the oxygen K-edge were measured with the improved apparatus at different amounts of exposure and the results are shown in fig. 3. Characteristic features between oxygen in a chemisorbed state and in an oxidizing one are clearly distinguishable. These data should be useful for finger printing.

The determination of inter-atomic distance in a solid should be a main subject in the study on EELFS. The EXELFS for a 200 L oxygen-exposed surface with the c(2 × 2) structure was measured with a detector that collects scattered electrons at an angle θ_{inc} of 5° to the surface plane, using primary electrons at an energy E_{p} of 2500 eV incident at a grazing angle θ_{out} of 5° on the plane of the surface. Thus obtained data, after being background subtracted, were Fourier-transformed into radial distribution curves, using theoretically estimated phase shifts [15]. The inter-atomic distance between adsorbing oxygen and nickel on the outermost layer was found to be 0.196 nm. This value can be compared with 0.195–0.197 nm from SEXAFS [19,20].

As described before, the variation of momentum transfer in EELFS corresponds to those of polarization in XAFS. The orientation of momentum transfer

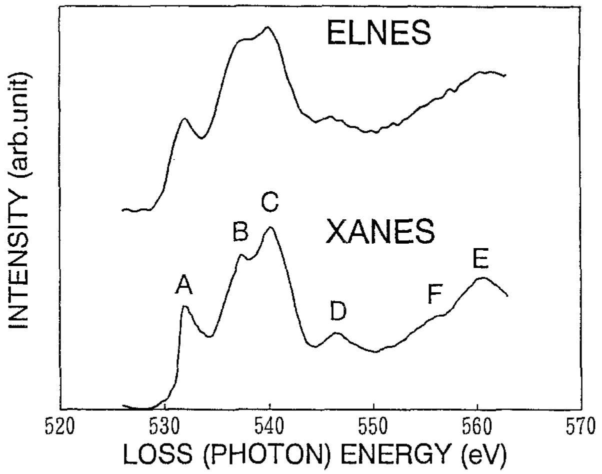

Fig. 2. Comparison between the ELNES and the XANES spectrum of oxygen K-edge for a cleaved NiO(100) surface [17,18].

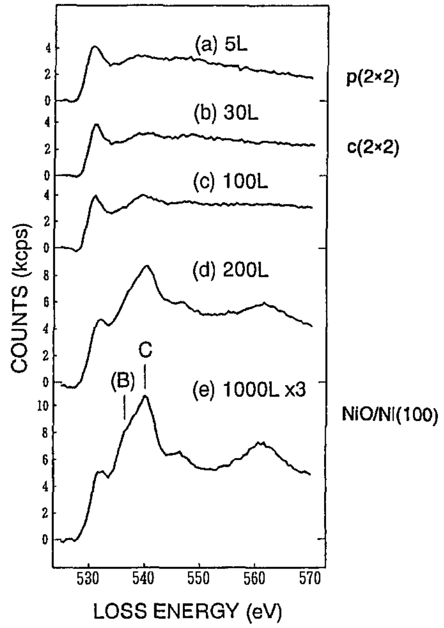

Fig. 3. Variation of ELNES oxygen K-edge spectra for an oxygen-covered Ni(100) surface as a function of oxygen exposure.

can be varied by adjusting incident electron energy E_p and scattering angle which is given as the sum of θ_{inc} and θ_{out} defined above. The oxygen K-edge ELNES for the p(2 × 2) surface with the different orientations of momentum transfer were measured. These are compared to those of XANES in fig. 4. The XANES spectra were measured at grazing and normal incident angles [21]. The ELNES spectra show rather splendid correlation with the XANES results.

Another example from the results is the irradiation effect of probe electron on adsorbate-covered surfaces. Fig. 5 is the variation of spectra for the Ni(100)-c(2 × 2)–O and the NiO/Ni(100) surfaces, caused by the continuous irradiation of electrons during the measurement. The original shape gradually changes to that of NiO/Ni(100). The conversion is rather remarkable, and this could be attributed to the induced desorption of oxygen by irradiation of primary electrons. It is estimated from fig. 5 that half of the initial number of adsorbates would be desorbed with the irradiation of 2.8 keV electrons at a current density of 4 $\mu A/mm^2$ for 8 h duration. In contrast to a Ni(100)-c(2 × 2)–O surface, the spectrum of NiO/Ni(100) did not change its structure at all under the same condition. This suggests that the NiO layer should be highly stable even under a heavy electron irradiation.

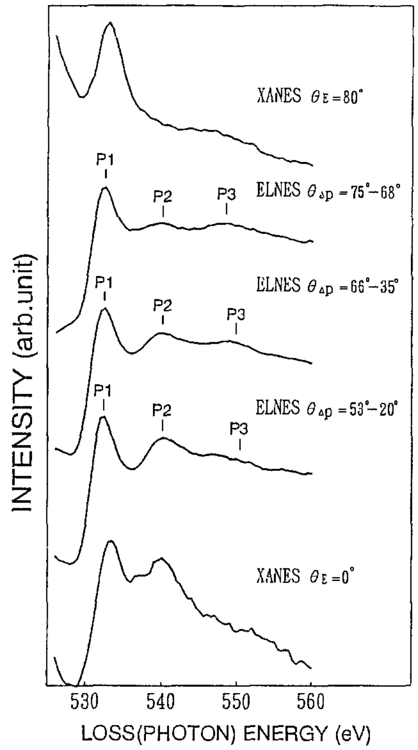

Fig. 4. Angle resolved ELNES spectra using the equivalent relation of momentum transfer in EELFS to polarization in XAFS [17,18]. The direction of momentum transfer Δp is denoted as $\theta_{\Delta p}$. $\theta_{\Delta p}$ were settled with the following factors θ_{inc}, θ_{out} and E_{p}. See text for definitions. θ_{inc}, θ_{out}, $E_{\mathrm{p}} = 12°, 3°, 2.8$ keV for $\theta_{\Delta p} = 75°–68°$; 4°, 6°, 2.8 keV for $\theta_{\Delta p} = 66°–35°$; and 3°, 3°, 2.0 keV for $\theta_{\Delta p} = 53°–20°$. $\theta_{\Delta p}$ and θ_E are angles to the plane of a sample surface.

4.2. OXYGEN ON W(100)

Being measured as a function of exposure, the peak to peak height of the oxygen KLL Auger spectrum formed a slight dip in the oxygen exposure ranging from 3 to 5 L. Then, the EELFS observations were carried out by changing the oxygen exposure, to obtain inter-atomic distances between oxygen and tungsten as a function of exposure. The results, as shown in fig. 6, indicate a rather drastic dispersion in that range of exposure, where the anomaly of the oxygen KLL Auger peak height appeared. It should be noted that except for the above range, the observed inter-atomic distance takes a nearly constant value of 0.165 nm [22]. This may suggest that adsorbed oxygen would be so movable at the above population that it could occupy more stable positions under the top layer.

The adsorption of oxygen on W(100) has been extensively investigated with the interest in its adsorption kinetics. The proposed model by Germer and May is the surface reconstruction caused by replacing oxygen atoms with tungsten atoms

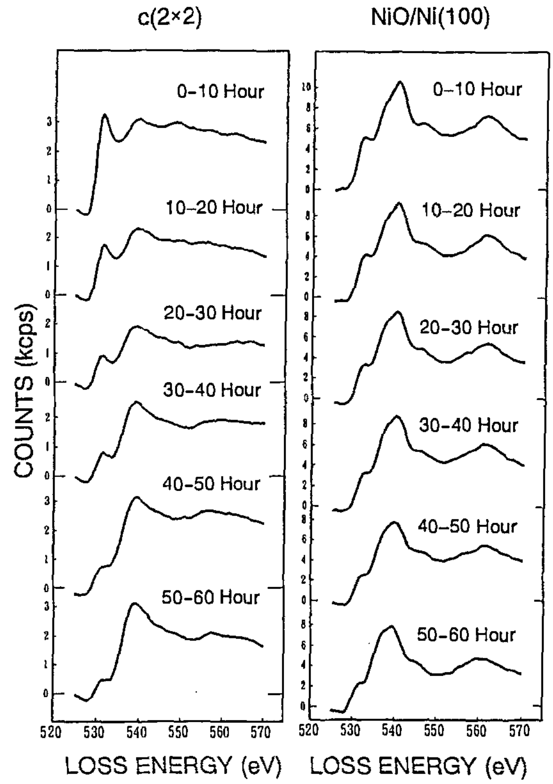

Fig. 5. Induced variations of ELNES spectra for Ni(100)-c(2 × 2)-O and NiO/Ni(100) surfaces by irradiation of probe electrons [17].

underneath [23]. Later, however, Bauer and coworkers proposed that oxygen atoms stay on the top layer at a temperature below about 600 K [24,25].

The present results seem to support Germer and May's model. However, the interaction of oxygen with tungsten on a surface seems to be affected seriously even by slight variations in surface conditions, such as caused by defect, contamination, temperature change and also by excitation with irradiation of energetic particles. Therefore, it is needed to do investigations in detail under more strict control of experimental conditions to reach definite conclusions.

The similar experiment for nitrogen adsorption on a tungsten (100) surface has also been investigated. The results will be reported in a different paper [22].

5. Conclusion

The apparatus for characterizing local structures in solids have been developed by making modifications in a conventional electron energy-loss spectrometer. Although they fulfill almost similar performance to an equipment for measuring

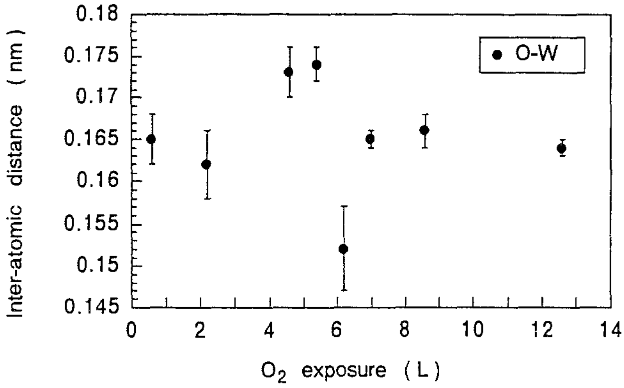

Fig. 6. Plot of the inter-atomic distances between adsorbed oxygen and nearest-neighbor tungsten for an O/W(100) surface, which were determined from EELFS spectra as a function of oxygen exposure [22].

XAFS, one can construct these apparatus at small-scale home laboratories just like widely used electron spectrometers. It is essential from the theoretical point of view to measure the energy-loss fine structure by detecting the forward-scattering electrons at a grazing angle. In case of oxygen adsorption on a Ni(100) surface, the inter-atomic distance between oxygen and the nearest neighbor Ni atom could be determined and variations in the ELNES for Ni surface with different oxygen-coverage were also clearly observed. The angle-resolved spectrum is available by adjusting the orientation of momentum transfer for scattered electrons. On the O/W(100) system, the distance between oxygen and the nearest tungsten atom was found to vary in a specified range of oxygen exposure.

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