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Soft x-ray diffraction anomalous fine structure on Ni/V multilayers

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Abstract. We report on anomalous soft x-ray scattering experiments on Ni/V multilayers. The fine structure above the $L_{2,3}$ absorption edges of V, observed using the first order multilayer reflection, can be interpreted as diffraction anomalous fine structure (DAFS), from which information on the local structure of V can be obtained. This interpretation is in agreement with extended x-ray absorption fine structure (EXAFS) results obtained in transmission mode on a similar Ni/V multilayer. The results demonstrate that the DAFS technique can be employed for multilayer analysis in the soft x-ray region in a similar fashion as for crystalline materials in the hard x-ray region.

Since the development of synchrotron radiation sources for production of intense and highly collimated radiation with a continuous wavelength distribution, techniques based on x-ray absorption spectroscopy (XAS) have been strongly improved and are commonly used today in a variety of scientific fields. XAS provides information on the electronic states of the absorbing ion, from the x-ray absorption near edge structure (XANES) [1], as well as information on the local structure of the surrounding ions from the extended x-ray absorption fine structure (EXAFS) [2]. One of the drawbacks of XAS techniques is that the available information is averaged over all ions of the same atomic species in the sample. Therefore, it is impossible to separate the contributions from identical ions occupying different sites. In addition, it is difficult to differentiate between the contributions from thin layers or buried layers and those from substrates or cap layers containing the same atomic species. A newly developed technique, diffraction anomalous fine structure (DAFS) [3], overcomes these problems by using the diffraction condition to select a subset of resonant atoms, based on their long-range order or unique lattice parameter. DAFS consists of a measurement of the intensity of Bragg reflections as a function of energy at and above an absorption edge of the ion of interest. It has been shown that this technique allows site specific XAS information to be obtained and that it can be used to study buried layers [3–5]. The use of DAFS has so far been limited to the hard x-ray region, because for longer wavelengths most compounds do not contain Bragg reflections within the Ewald sphere.

Multilayers have important applications in x-ray optics as well as for magnetic storage media. They often have lattice spacings (d) in the range of tens to hundreds of ångströms and therefore show Bragg reflections in the soft x-ray region, thus they may be characterized with both hard and soft x-ray radiation. The Ni/V multilayers under consideration here are part of an ongoing development for soft x-ray optical elements such as reflection polarizers and transmission phase retarders [6, 7].

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Here we present soft x-ray diffraction results at and above the V $L_{2,3}$ edges of Ni/V multilayers. We show that smooth modulation in the Bragg intensity above the V $L_{2,3}$ edges can be interpreted in terms of the modification of the scattered x-ray intensity by the interaction of virtual photoelectrons with the surrounding ions (DAFS). These findings are compared with transmission EXAFS and are used to characterize the vanadium component in the Ni/V multilayers. To our knowledge, this is the first time that DAFS is reported in the soft x-ray region.

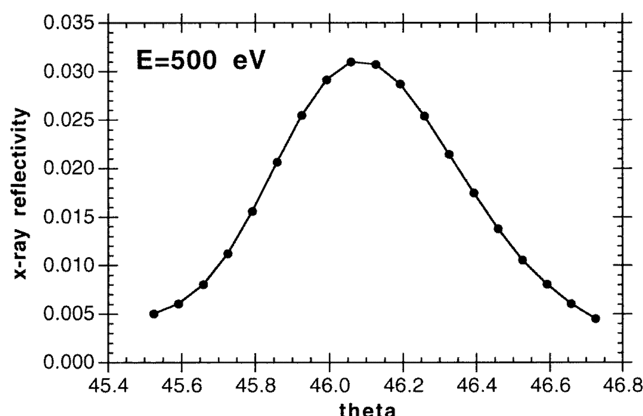

Figure 1. Normalized $\theta/2\theta$ scan taken at 500 eV of the 150 bi-layer Ni/V reflection multilayer.

Films of 150 and 200 bi-layers of Ni/V were deposited by magnetron sputtering at room temperature, for the reflection and transmission multilayers, respectively. A silicon wafer of 76 mm diameter was the substrate for the reflection multilayer, and 1200 Å of Si_3N_4 was the substrate for the transmission multilayer [7]. The individual layer thicknesses were nominally 60% V and 40% Ni, with a bi-layer period $d = 17.2$ Å, based on monolayer growing rates. An aluminium cap of approximately 30 Å thickness was added to inhibit oxidation of the top layers. More details about the sample preparation can be found in [7]. The multilayers were characterized by Cu Kα radiation, with which multilayer Bragg peaks were observed up to third order. A bi-layer thickness of $d = 17.3$ Å was obtained by fitting the Cu Kα data.

The soft x-ray scattering and transmission experiments were performed with the reflectometer at the PM 4 beamline of BESSY. A value of $c_{ff} = \cos\alpha/\cos\beta = 2.25$ (α, β are the incident angles on the grating) for the SX700 type monochromator [8] was chosen, and an Fe filter of 0.75 μm thickness on 0.3 μm parylene was inserted into the incoming beam for the suppression of higher order harmonics.

Figure 1 shows the results of a $\theta/2\theta$ scan taken at 500 eV. Because the following analysis uses only the maximum peak intensity, a relatively short $\theta/2\theta$ range with small step size was chosen. X-ray reflectivity at the peak maximum, and transmission data of the 200 bi-layer Ni/V multilayer in the range of 450 to 750 eV, are shown in figure 2. The smooth increase of the peak intensity well below the V $L_{2,3}$ edges is due to the strongly increasing contrast between the atomic scattering factors f' of V and Ni. The first, second and third maxima of the reflectance can be associated with the V L_3, V L_2 and the oxygen K edges at 512, 521 and 535 eV, respectively. The appearance of a peak at the oxygen K edge indicates, as for the V L_3 and V L_2 edges, that the difference in the f' values between the V and Ni layers goes through a maximum (see equation (2)). Therefore, the enhanced intensity at the

oxygen K edge can be interpreted in terms of differing amounts of oxygen incorporated into the V and Ni layers. From the standard reduction potentials, one would predict that oxygen is predominantly incorporated into the V layers. In other words, the oxygen in the V layer reduces the scattering length of the layer at the oxygen K edge, which increases the contrast between the layers as before the V $L_{2,3}$-edges. However, the absence of an observable dip in the transmission data indicates that the amount of oxygen in the layer is small. We note that for the absorption experiment, the signal is strongly dominated by the absorption of V and is therefore not sensitive to a small amount of oxygen, whereas the diffracted intensity is proportional to the difference of the similar scattering lengths of V and Ni, which is more sensitive to oxygen contamination. Above these edge features, smooth variations in both the diffraction and the transmission signals are observed (figure 2), which we interpret as DAFS and EXAFS, respectively.

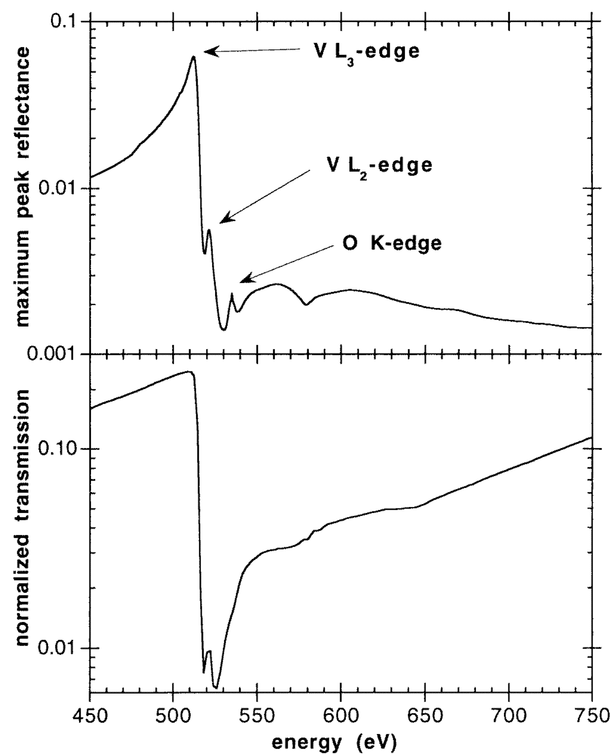

Figure 2. The maximum peak reflectance of the 150 bi-layer Ni/V reflection multilayer (upper part) and the transmission of the 200 bi-layer Ni/V transmission multilayer (lower part).

The structure factor for x-ray diffraction can be written as [4]

$$F(Q,E) = \sum_n (f_0 + f_s' + \mathrm{i} f_s'')\,\mathrm{e}^{\mathrm{i}Qr_n} + \sum_l (f_{0s}''\chi' + \mathrm{i} f_{0s}''\chi'')\,\mathrm{e}^{\mathrm{i}Qr_l} \qquad (1)$$

here n is the sum over all atoms and l the sum over the atoms contributing to the resonance, where f_0, f' and f'' correspond to the fundamental, real and imaginary parts of the smoothly varying scattering lengths, f_{0s}'' to the imaginary part of the electronic transition alone, and χ' and χ'' to the real and imaginary part of the oscillatory contribution.

For the analysis of the DAFS data of a multilayer, the structure factor and the crystallographic weights are replaced by those of the multilayer. Assuming that the sample is an ideal, infinite multilayer with period d and with individual layer thicknesses $a = \varepsilon d$ and $(d - a)$, the structure factor [9] is given by

$$F = (f_{Ni} - f_V)(\mathrm{e}^{\mathrm{i}\varphi} - 1)/2\pi m\mathrm{i} \qquad \varphi = aq_z = 2\pi\varepsilon m \tag{2}$$

where m is the order of the reflection, $q_z = 2\pi m/d$ the perpendicular part of the scattering vector and f_{Ni} and f_V include all three contributions to the scattering length. The factor of i in the denominator can be neglected since it corresponds to an overall phase factor which is independent of the reflection. To simplify the following extraction and analysis of the DAFS signal from the data, we assume $\varepsilon = 0.5$, which leads to a purely real structure factor. The intensity can then be simplified to

$$I(E) = |F_0|^2 + 2|F_0|(f'_a(E) + f''_{a0}\chi'(E)) + \text{ higher order terms} \tag{3}$$

where $|F_0|$ corresponds to the energy independent part of the structure factor. The deviation from $\varepsilon = 0.5$ introduces a small error, leading to small uncertainties in the determination of the local structure parameters because it leads to a complex structure factor and to some admixtures form the imaginary part of χ in the DAFS data, which distinctly complicates the data analysis.

For the analysis of the total intensity, the structural Debye–Waller factor (e^{-2M}) has also been included, since it reduces significantly the intensities of the Bragg peaks from multilayers due to roughness and interdiffusion. Equation (3) shows that $I(E)$ contains a term proportional to $\mathrm{Re}(\chi) = \chi'$, which corresponds to a $-\pi/2$ phase shift with respect to the $\mathrm{Im}(\chi) = \chi''$ from EXAFS. The background was found to be less than 1% and was hence neglected. To correct for absorption in the scattered intensity, we extracted the energy-dependent absorption coefficient $u(E)$ from the transmission data; the absorption-corrected near-edge absorption fine structure of the diffraction data was normalized by the spline method [4]. The transmission data were treated similarly, as is standard procedure for EXAFS [2]. Due to the overlap of the L_2- and L_3-edge data, the normalized data have an amplitude which is approximately a factor of two too small, requiring a later correction. For the analysis of the EXAFS data, the influence of the V L_1 edge was calculated and found to be small; for the DAFS, the influence on the data is even less, due to the strong dependence on f', which remains approximately constant over the L_1 edge. The DAFS data were therefore phase-shift corrected, allowing data analysis with a standard EXAFS analysis code (EXAFSPAK).

To obtain information on the local structure of the interfaces with DAFS, differences in the structure factor for the bulk and interface contributions for different multilayer reflections are required. In an idealized model, with scattering length f_x from position 0 to x (interface thickness x), f_a from x to $x + a = d/2$, f_x from $d/2$ to $d/2 + x$ and f_b from $d/2 + x$ to d, the bulk and interface part of the structure factor are proportional to

$$\begin{array}{lll} F_{bulk} \propto \mathrm{i}(f_b - f_a)(1 + \mathrm{e}^{\mathrm{i}\varphi}) & F_{interface} = 0 & \text{for } m \text{ odd} \\ F_{bulk} \propto \mathrm{i}(f_a + f_b)(1 - \mathrm{e}^{\mathrm{i}\varphi}) & F_{interface} \propto 2\mathrm{i}f_x(1 - \mathrm{e}^{\mathrm{i}\varphi}) & \text{for } m \text{ even} \end{array} \tag{4}$$

where $\varphi = 2\pi mx/d$ and f_x is a function of f_a and f_b. In the ideal case ($x = 0$), all multilayer peaks with even m vanish. In the case of small non-zero x and for reflections with even m, the contributions to the DAFS from the bulk and the interface are similar, whereas for small x and reflections with odd m, only the bulk contributes. In principle, therefore, DAFS can exhibit an interface sensitivity by choosing different multilayer Bragg peaks. However, it is difficult to extract local structural information, since an accurate model of the scattering length distribution of the interface is required. We note that the study by Renevier *et al* [5] has demonstrated that

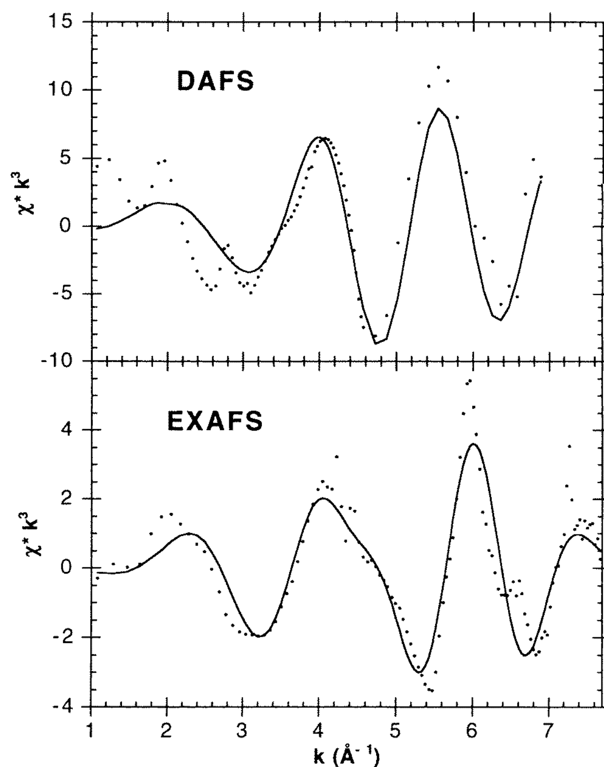

Figure 3. Phase shifted k^3 V $L_{2,3}$-edge diffraction anomalous fine structure data for the 150 bi-layer Ni/V reflection multilayer (upper part) and k^3 V $L_{2,3}$-edge EXAFS data of the 200 bi-layer Ni/V transmission multilayer (lower part). The dotted lines correspond to the data and the full lines to the fit.

it is indeed possible to obtain local structural information on the interface of epitaxially grown multilayers. In principle, a sufficiently detailed model would yield information on the interface of non-crystalline multilayers, but such a study is beyond the scope of the work presented here.

Figures 3 and 4 show the extracted DAFS and EXAFS data and the corresponding Fourier transforms, respectively. For the DAFS, a single first shell distance is observed, whereas for the EXAFS, intensity from a second shell is detected. A thick V layer (500 Å), sputtered under the same conditions as the reflection multilayer, did not show crystallographic Bragg reflections during characterization with Cu Kα radiation, indicating that the layer is amorphous. Therefore, we do not have any *a priori* information on the atomic structure of this layer. The DAFS data are very limited in k-space because the diffracted intensity already strongly increases approximately 100 eV below the Ni $L_{2,3}$ edges, again due to the contrast in the atomic scattering factor f' between Ni and V at these energies. We note that the DAFS is proportional to F_0 which is proportional to $(f_a - f_b)$, whereas the diffraction intensity is proportional to $|F_0|^2$ which is proportional to $(f_a - f_b)^2$. For $\chi(E)$ of the DAFS and EXAFS data, the atomic amplitudes and phases of the V L_2 and L_3 edges are approximately the same, with E_0 values differing by only 7 eV. Therefore in the region of interest ($k > 2$ Å^{-1}), the $\chi(E)$ add almost coherently, which corrects for the factor of two from the normalization procedure and leads to

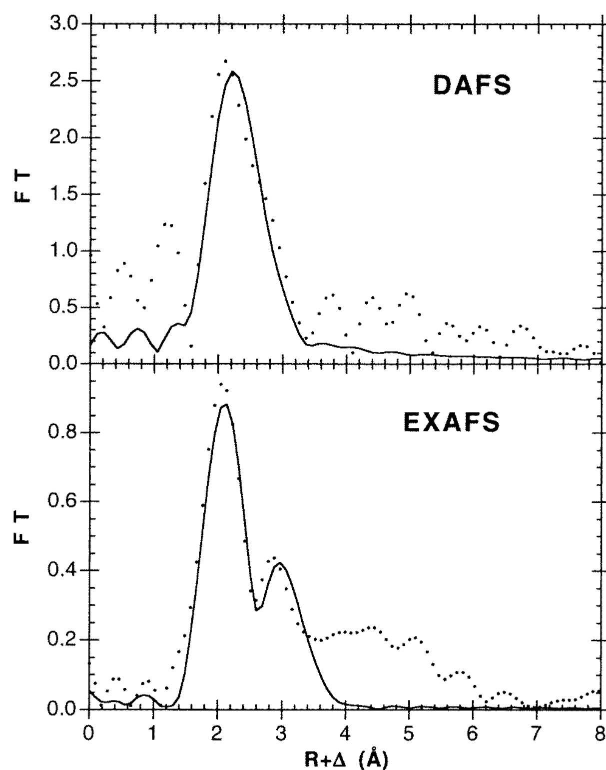

Figure 4. Fast Fourier transforms of the V $L_{2,3}$-edge DAFS and EXAFS of the 150 bi-layer Ni/V reflection multilayer (upper part) and of the 200 bi-layer Ni/V transmission multilayer (lower part). The dotted lines correspond to the data, and the full lines to the fit.

a renormalized E_0 and R when describing the data as originating solely from the V L_3 edge. The atomic phase shifts and amplitudes are calculated using FEFF7 [10]. For the EXAFS data, a second shell V–V distance has been added. The corresponding parameters are given in table 1 and compared with results from a fit with a fixed number of nearest neighbours in the metallic body-centred cubic (bcc) V phase.

The large crystallographic Debye–Waller factors retrieved from the DAFS and EXAFS fits indicate that V is in a disordered state in these very thin layers. The first shell distances of the DAFS and EXAFS data differ outside the error bars and both are slightly smaller than those of bcc V metal. The difference between EXAFS and DAFS may be related to slight differences in the sputtering conditions for the two multilayers or due to the simplification of our model by the choice of $\varepsilon = 0.5$ (equal thicknesses of the layers). In addition, the most consistent description for the Debye–Waller factors is obtained with a smaller number of nearest neighbours and a larger number of next-nearest neighbours, again indicating distinct deviations in the local structure from metallic V. It is likely that the small amount of impurity oxygen in the V layer is responsible for the amorphous structure of the layer.

In conclusion, we have presented soft x-ray diffraction experiments on the first-order Bragg reflection of an Ni/V multilayer at the V $L_{2,3}$ edges. We were able to show that the intensity variation of the peak maxima above the edges can be interpreted as diffraction anomalous fine

Table 1. Structural parameters from the DAFS and EXAFS fits for the 150 bi-layer Ni/V (DAFS) and the 200 bi-layer (EXAFS) multilayer Ni/V, compared with those for bcc V metal. The abbreviations 'fs' and 'ss' denote the first and second shell, respectively.

	N	σ^2 (Å^2)	R (Å)	E_0 (eV)
DAFS fs	6	0.023(3)	2.37(8)	−8(3)
EXAFS fs	6	0.025(1)	2.23(5)	−10(2)
EXAFS ss	8	0.026(2)	3.20(5)	−10(2)
EXAFS bcc fs	8	0.030(1)	2.22(5)	−10(2)
EXAFS bcc ss	6	0.021(2)	3.18(5)	−10(2)
V bcc fs	8	—	2.62	—
V bcc ss	6	—	3.03	—

structure, similar to the DAFS of crystallographic Bragg reflections in the hard x-ray region. The results obtained on the local structure are in agreement with those from transmission EXAFS. We thereby demonstrate that DAFS can be successfully performed on multilayers in the soft x-ray region and that it represents a possible option to obtain information on the local structure of multilayers and their interfaces, not accessible with conventional EXAFS. We believe that DAFS in the soft x-ray region will assist in the characterization of the local structure of multilayers containing light elements such as O and C, either as normal constituents or as impurities.

Acknowledgments

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