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NEW CORRECTION PROCEDURE FOR X-RAY SPECTROSCOPIC FLUORESCENCE DATA: SIMULATIONS AND EXPERIMENT

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ABSTRACT

X-ray fluorescence spectroscopy is a widely used method for determining the electronic configuration and local structure of dilute species with high sensitivity. In the dilute limit, and for thin films, the X-ray fluorescence signal is directly proportional to the atomic sub-shell absorption coefficient. However, for concentrated samples, the well-documented self-absorption effect often leads to the severe suppression of XANES (X-ray Absorption Near-Edge Structure) and EXAFS (Extended X-ray Absorption Fine-Structure) amplitudes. Thus to recover the real value of the sub-shell absorption coefficient, it is important to apply correction procedures to the measured fluorescence spectra. In this paper, we describe a new straightforward method to correct for self-absorption effects (the difference in the measured fluorescence signal compared to that of the true sub-shell photoabsorption coefficient) in XANES and EXAFS fluorescence measurements. Using a variety of sample and detector configurations, this method is used to extract the sub-shell absorption coefficient on elemental nickel and thick single-crystals of $Gd_3Ga_5O_{12}$ and $LaAlO_3$.

INTRODUCTION

Since its development by Jaklevic et al. [1], fluorescence EXAFS and XANES measurements are standard techniques for examining the local and electronic structure of dilute species at synchrotron radiation sources. X-ray fluorescence spectroscopy applied to dilute species has high-sensitivity and yields distortion-free results. However, when concentrated samples cannot be made thin enough for transmission-based experiments (e.g for single-crystal and brittle specimens), the X-ray fluorescence (or electron yield) mode of detection is required. Unfortunately for concentrated samples, X-ray fluorescence spectra are often highly distorted due to self-absorption effects and corrections are required to recover the real value of the sub-shell absorption coefficient. The effect of self-absorption on the measured X-ray fluorescence EXAFS intensity has been described in many papers over the past two decades [1-11]. The total normalized background-subtracted fluorescence intensity, ignoring refraction effects at the sample boundary, is given by,

$$\frac{I_f}{I_o}=K\frac{\mu_{sub}}{\left[\mu_{tot}+\frac{\mu_f \sin\theta}{\sin\phi\cos\tau}\right]}\left(1-e^{-\left[\frac{\mu_{tot}}{\sin\theta}+\frac{\mu_f}{\sin\phi\cos\tau}\right]D}\right) \tag{1}$$

where, I_f and I_o are the fluorescence and incident x-ray intensities, respectively, and K is a calibration constant. μ_{sub} is the sub-shell linear photoabsorption coefficient, μ_{tot} is the total

linear photoabsorption coefficient that includes both the atomic sub-shell being probed and the absorption due to other electronic states within the sample ($\mu_{tot} = \mu_{sub} + \mu_{other}$), and μ_f is the total linear absorption coefficient at the characteristic fluorescence energy. θ is the angle of X-ray incidence with respect to the sample surface, ϕ and τ represent the angles of fluorescence detection, and D is the sample thickness. The only difference in this equation (from those found in prior self-absorption correction papers) is the additional $\cos\tau$ term, which can be used, in accompaniment with the $\sin\phi$ term, to correct for self-absorption effects using large area detectors. It is evident by examining Equation 1 that self-absorption is strongly dependent upon the concentration of the species under investigation (through the linear absorption coefficient), the thickness of the sample and the experimental geometry. In the EXAFS region, it has been shown that self-absorption effects can be minimized or corrected for (i) using normal-incidence grazing take-off geometries [5,8,9], (ii) on thick and concentrated samples [4,7,10,11] and (iii) on intermediate thin film thicknesses [3]. A general correction procedure for fluorescence EXAFS also has been described by Booth and Bridges [2], and the extension of the correction procedure for thin sections, explicitly for the XANES region, has also been demonstrated [6].

NEW X-RAY FLUORESCENCE SELF-ABSORPTION CORRECTION PROCEDURE

The new correction procedure we describe is valid through the entire XANES and EXAFS spectral range, and is applicable for any sample configuration and experimental geometry. By subtracting the background from the fluorescence spectra and normalizing, the calibration constant K (Equation 1) can be determined. Subsequently, through knowledge of the experimental/sample parameters and the well-defined atomic-like absorption coefficient far from resonance (where EXAFS oscillations can be ignored), the real value for the sub-shell photoabsorption coefficient can be obtained by solving Equation 1 numerically. The steps in completing this self-absorption correction procedure are described below:

a) Incident X-ray intensity measurements: By measuring the current from an ionization chamber placed upstream of the sample, the X-ray photon intensity at the sample location can be calculated through (i) knowledge the ionization potential of the fill-gas (ii) use of the energy-dependent absorption coefficients of the fill-gas (obtained from the x-ray data tables), and (iii) applying absorption corrections for any additional flight-paths. This step is very important for accurate normalization and background subtraction in the subsequent steps.

b) Background subtraction and normalization: Background from scattering processes (and other fluorescence channels) provides an additional component to the measured fluorescence intensity that can produce inaccurate results in the self-absorption correction procedure. However, it is possible to significantly minimize the background and thus reduce its contributions to the measured fluorescence signal. Background minimization can be achieved by performing the experiment in the plane of the storage ring and at ninety-degrees to the incident radiation, by using an energy-dispersive detector with good energy resolution or a crystal analyzer (to separate the fluorescence from the background), and employing good detector collimation. Once the background has been determined, it can be normalized and subtracted from the normalized fluorescence intensity and Equation 1 can be applied.

c) Determination of atomic-like sub-shell absorption coefficients: To solve Equation 1, it is necessary to include the absorption coefficient from the "non-resonant" electrons (μ_{other}). These contributions are smooth and atomic-like and are not related to the absorption edge under

investigation. The total atomic-like photoabsorption coefficients are readily available from the x-ray data tables, from which μ_{other} can be extracted. The total absorption coefficient of the single-energy X-ray emission channel (μ_f) can also be obtained from these tables.

d) Determination of calibration factor and extraction of absorption coefficients: The calibration factor K is calculated by substituting the atomic-like absorption coefficients (step c), the experimental geometry angles and sample thickness into Equation 1. The sub-shell photoabsorption coefficient (μ_{sub}) can now be obtained numerically at each x-ray energy data-point. In this procedure, trial values of μ_{sub} are entered into Equation 1, and the output is compared with the measured background-subtracted normalized fluorescence intensity, with the best value of μ_{sub} being accepted. In our preliminary algorithm, trial values of μ_{sub} where input sequentially from 0 cm^{-1} (below threshold), in unit steps, up to the value where agreement was reached. For a typical fluorescence spectra, ~ 10^3 trial-values of μ_{sub} at each energy point are required, with ~10^3 data points (e.g. 1 keV wide spectra, with 0.5 eV steps). Obviously, improvement to this algorithm can be obtained by restricting the starting value of μ_{sub} (a starting of zero is not required above threshold) and by employing a more sophisticated 'search' procedure for μ_{sub}.

SIMULATIONS OF SELF-ABSORPTION EFFECTS ON ELEMENTAL NICKEL

To highlight the detrimental effect of self-absorption on X-ray fluorescence spectra, X-ray transmission data on a 7 μm thick nickel foil were collected at the National Synchrotron Light Source (NSLS) X23A2 National Institute of Standard and Technology (NIST) XAFS beamline (see following section for details). The linear photoabsorption coefficient at the Ni K-edge (8.333 keV) was obtained by subtracting the pre-edge region from the transmission data and normalizing to the atomic-like value away from resonance (at 9 keV). This data was then fed into Equation 1, and simulated X-ray intensities at normal incidence ($\theta=90^o$) for the Ni Kα fluorescence line (7.470 keV) were computed for various sample/detector configurations. The values for the atomic-like linear absorption coefficients for determination of the calibration factor were μ_{tot} (9 keV)=2429 cm^{-1}, μ_{sub} (9 keV)=2125 cm^{-1} and μ_f (7.47 keV)=514 cm^{-1}. Figure 1; (i) Top-Left: this plot shows the effect of the detector geometry (angle of fluorescence take-off), as ϕ is varied from 2° to 79° on a 7 μm thick nickel foil. As shown, self-absorption effects are reduced at grazing-exit take off as previously demonstrated. [5, 8, 9] (ii) Top-Right: this plot shows the effect of self-absorption as the nickel thickness is varied from 1 μm – 50 μm at grazing-exit take-off. As shown, the effect of sample thickness is quite small due to the grazing-exit geometry employed. (iii) Bottom-Left: this plot depicts the effect of self-absorption as the nickel thickness is varied from 1 μm – 50 μm with a take-off angle of 45°. Evidently, self-absorption increases as the sample becomes thicker.

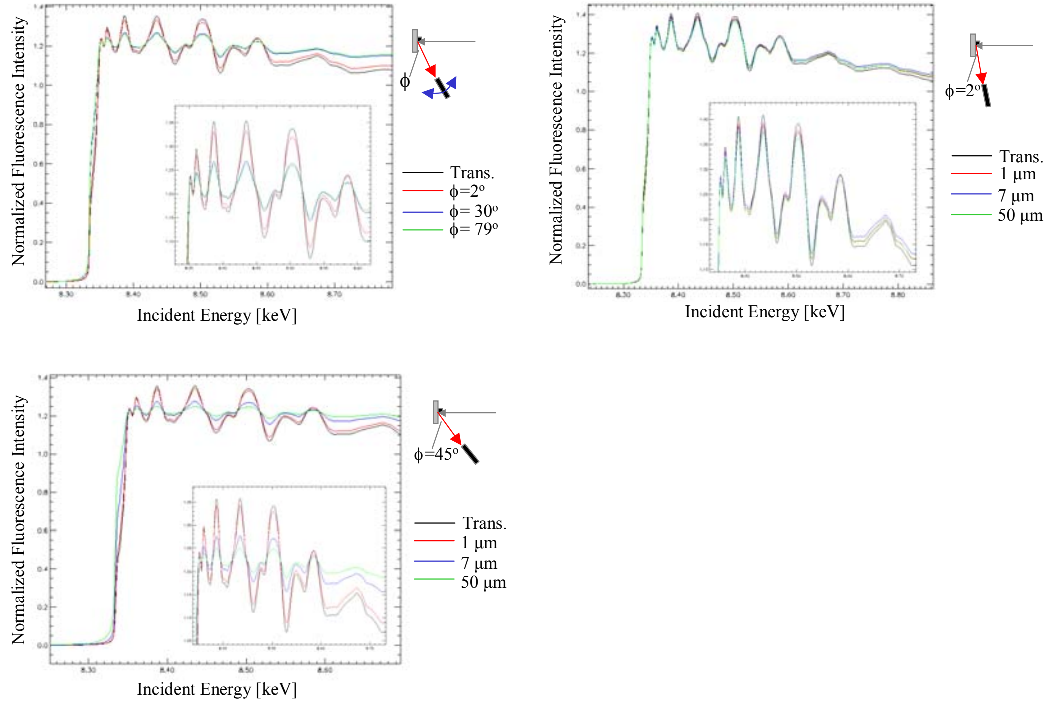

Figure 1: Simulated X-ray fluorescence intensities at normal incidence on nickel.

EXPERIMENTAL SELF-ABSORPTION CORRECTIONS

The self-absorption correction procedure were applied to a variety of different sample and experimental configurations. Experiments were performed on elemental nickel foils and thick single crystal $Gd_3Ga_5O_{12}$ at the NSLS X23A2 XAFS (Si(311) monochromator) beamline, and on thick single-crystal $LaAlO_3$ at the UNICAT 33-BM beamline (Si(111) monochromator) at the Advanced Photon Source, as described below:

a) Self-absorption correction on nickel at NSLS X23A2: The experimental geometry consisted of two N_2-filled ionization chambers that were used to measure the incident and transmitted X-ray intensities. The sample and detector were mounted on a 2-circle goniometer (arranged in the horizontal plane) to enable rotation of both the θ and ϕ angles. The fluorescence intensity was recorded using an energy-dispersive detector (area=7mm^2) placed at 6 cm from the sample location and a multi-channel analyzer selected the required X-ray fluorescence line. The detector was operated in its linear range by reducing the total input counts through the addition of aluminum filters on its entrance window. The X-ray beam size at the sample position was 0.5 mm x 0.5 mm. Figure 2 shows the raw and self-absorption corrected Ni Kα X-ray fluorescence data taken on 7 µm (1 foil) and 28 µm (4 foils) thick nickel at normal incidence (θ=90°). The detector angle was varied between ϕ=10° and 79°, and transmission data are shown for comparison. As shown, the XANES and EXAFS amplitudes are severely suppressed in the raw data, even at a 10° take-off angle, but are recovered when self-absorption corrections are employed.

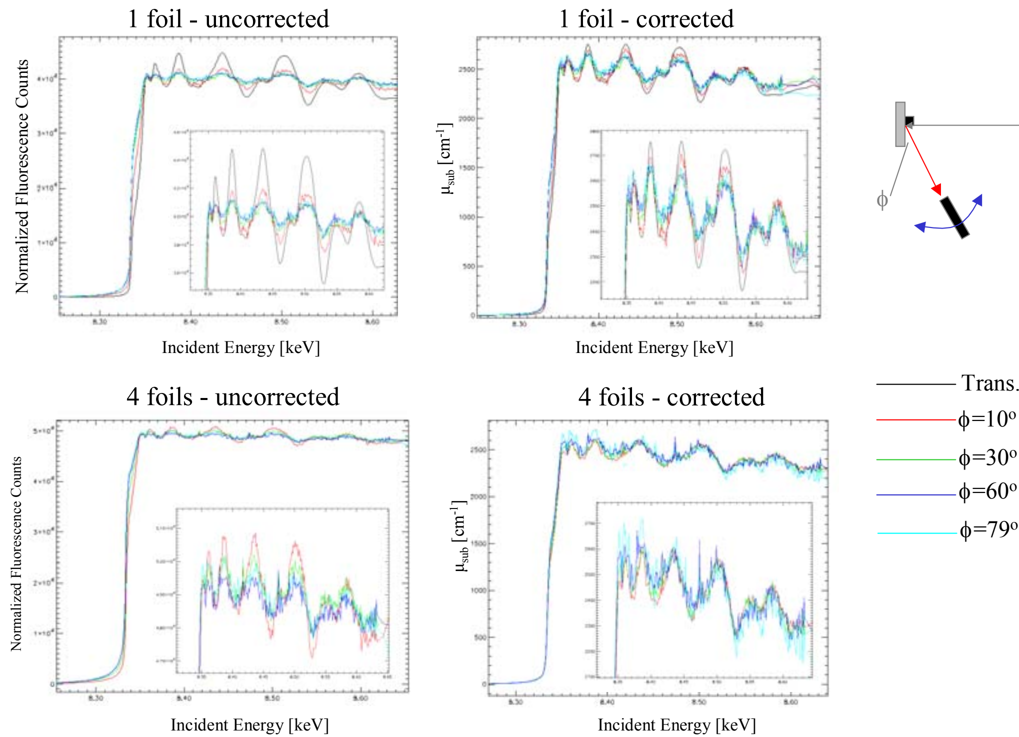

Figure 2: X-ray fluorescence spectra on nickel: raw (uncorrected) and self-absorption corrected spectra, at normal incidence and various detector take-off angles.

b) Self-absorption corrections on thick single-crystal $Gd_3Ga_5O_{12}$ at NSLS X23A2: The experimental arrangement was that as described in the previous section. X-ray fluorescence spectra on thick single crystal $Gd_3Ga_5O_{12}$ at the Gd L_3 absorption-edge (7.243 keV) were obtained by recording the intensity of the Gd Lα fluorescence line (6.057 keV). The density of the sample was taken as 7.07 g/cm^3 and the weight-fractions of the elemental components were Gd(46.6%), Ga(34.44%) and O(18.96%). The values for the atomic-like linear absorption coefficients for determination of the calibration factor were μ_{tot} (7.6 keV)=2041 cm^{-1}, μ_{sub} (7.6 keV)=1234 cm^{-1} and μ_f (6.057 keV)=1462 cm^{-1}. Figure 3 shows the raw and self-absorption corrected Gd Lα X-ray fluorescence data at normal incidence (θ=90°). The detector angle was varied between ϕ=10° and 79°. As shown in Figure 3, there is a strong dependence of the intensity of the white-line feature at the Gd L_3 absorption with take-off angle in the raw uncorrected data, and after self-absorption corrections are applied, the value of the linear sub-shell photoabsorption coefficient all agree.

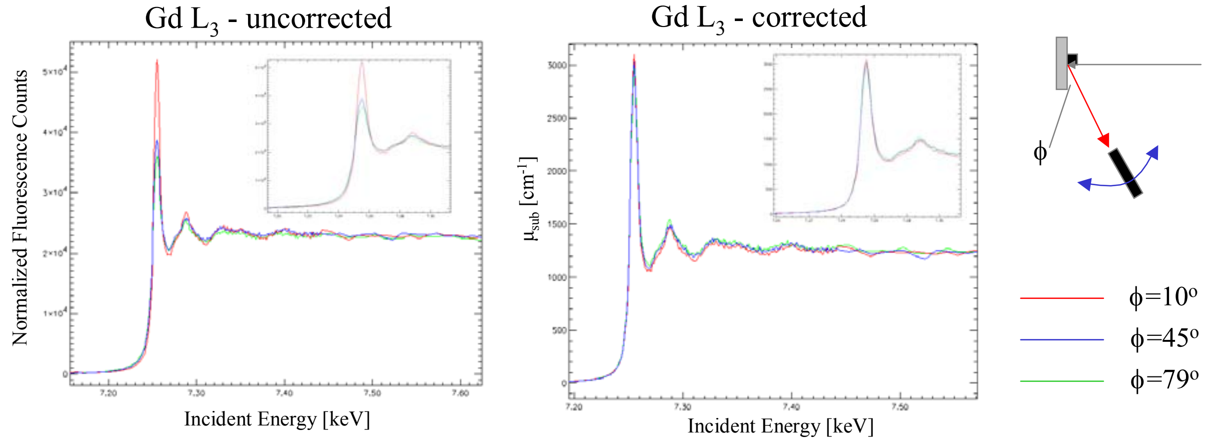

Figure 3: X-ray fluorescence spectra on thick single-crystal $Gd_3Ga_5O_{12}$: raw (uncorrected) and self-absorption corrected spectra at normal incidence and various detector take-off angles.

c) Self-absorption corrections on thick single-crystal $LaAlO_3$ at the UNICAT APS 33-BM beamline: This experiment was performed using a large-area argon-filled ionization chamber. In this case, Equation 1 was integrated over the range of ϕ and τ values, corresponding to the area of the detector ($\pm$ 50° vertically and 0$\rightarrow$50° horizontally). The sample was spun to eliminate Bragg reflections and arranged at normal-incidence. X-ray fluorescence spectra were recorded at the La L_3 absorption-edge (5.483 keV) and the La Lα fluorescence line (4.651 keV) was selected. The density of the sample was taken as 6.52 g/cm^3 and absorption due to aluminum and oxygen components were ignored. The values for the atomic-like linear absorption coefficients, for determination of the calibration factor, were μ_{tot} (5.78 keV) = 2041 cm^{-1}, μ_{sub} (5.78 keV)=1234 cm^{-1} and μ_f (4.651 keV)=1659 cm^{-1}. Figure 4 shows the raw and self-absorption corrected La Lα X-ray fluorescence data at normal incidence (θ=90°), and transmission data taken on $LaAlO_3$ powder for comparison. The difference in the intensity of the white-line feature at the La L_3 absorption edge, between the raw and corrected data, are very large and signifies the importance of applying self-absorption corrections. Agreement is found between the corrected fluorescence and transmission data other than for the region at the intense white-line, which appears to be overestimated by the correction procedure. We attribute this to the failure of not correctly accounting for absorption along the extraneous air flight-paths in the transmission measurement, and possible thickness-effects in the powder sample.

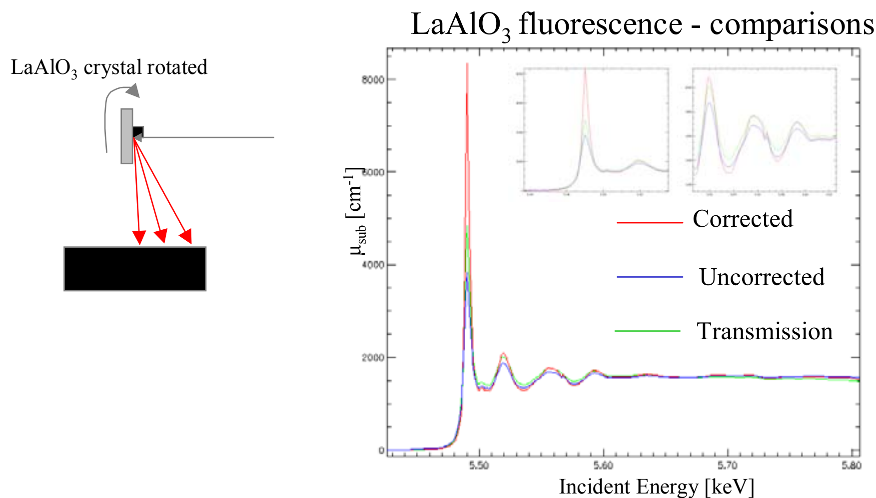

Figure 4: X-ray fluorescence spectra on thick single-crystal $LaAlO_3$ with a large-area detector: raw (uncorrected) and self-absorption corrected spectra at normal incidence.

CONCLUSION

We have described a new and straightforward self-correction procedure for fluorescence XANES and EXAFS data. The technique has been demonstrated on nickel foils and single-crystal specimens using both a small-area energy-dispersive detector and a large area ionization chamber. The importance of applying this correction procedure to fluorescence spectra taken on thick concentrated samples is essential, and its use at X-ray fluorescence microprobe beamlines would be most advantageous. We also note the importance of the development of X-ray fluorescence spectroscopy to the study of high-pressure phenomena in diamond-anvil cells, which this procedure is much suited to [12].

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