Development of the EXELFS technique for nano-scale atomic structure determination

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Abstract: EXELFS spectroscopy contains the same local atomic structural information as XAFS; furthermore, it is readily applied to low Z elements, has high spatial resolution, and the capacity of combining other local TEM measurements. Due to hitherto relatively poor quality of the EELS data, the EXELFS technique has not been developed to its full advantage until recently. We introduced various new methods to improve the data acquisition including real-time alignment and accumulation of virtually unlimited number of spectra while monitoring sample drift, radiation damage, and changes in energy resolution. We also developed a systematic data analysis procedure which corrects for the differences between EXELFS and XAFS, and adopts the UWXAFS data analysis software package to perform EXELFS data analysis with the same level of sophistication. The technique is demonstrated for SiC.

1 Background

Extended energy loss fine structure (EXELFS), like XAFS, is a unique technique for short-range order (sro) and atomic structure determination. It is element specific (measures partial pair distribution function, PPDF) and can be applied to amorphous, locally-ordered, and fully crystalline materials. While XAFS studies the fine structure of the x-ray absorption coefficient past an absorption edge [1], EXELFS does the same in the electron energy loss spectra (EELS) [2-5]. Both contain the same structure information.

EXELFS has the advantage over XAFS of greater spatial resolution (determined by the electron probe size) for investigation of spatially inhomogeneous samples such as in complex nanostructured materials. In addition, the sampled region can be characterized fully by other capabilities of TEM such as imaging, diffraction, and quantitative elemental compositional analysis.[6] The EXELFS technique is optimized for measuring losses in the 0-1500 eV range (soft X-rays) that is more difficult to investigate by XAFS using synchrotron radiation sources. On the other hand, EXELFS has disadvantages relative to XAFS of plural scattering corrections, limitations in measuring very dilute systems, and more stringent sample preparation requirements.

In spite of the ability to collect a spectrum of electron energy losses simultaneously (parallel detection [7]), the EXELFS technique has not yet been as fully optimized for structure determination as has XAFS. For example, to accurately measure the fine structure requires high counting statistics in EXELFS measurements. We have developed a systematic method to address the associated problems [8,9] and using this new method, one can now continuously acquire EELS data up to several hours to accumulate high enough counts (106 counts per channel or more) with minimum distortion in the spectra.

2 EXELFS data acquisition and analysis: problems and solutions

The following problems have been addressed [8-10]and the solutions have been incorporated into a newly developed software for EXELFS acquisition, called AcqLong [11], and analysis.

(1) Channel-to-Channel Gain Variation (CCGV): Due to CCGV in the parallel detector, systematic fluctuations can distort the data. By choosing an otherwise smooth part of the spectrum, the CCGV distribution can be calibrated by fitting a spline to the measured spectrum and dividing the subsequent data by this CCGV.

(2) On-line Acquisition of a Large Number of Spectra: The ability for increasing the counts/channel by increasing the single read-out time is limited because of energy drift, instability of power supply, environmental electrical and/or magnetic-field variations, instabilities in the electron source, mechanical vibrations, and saturation of the detector. The spectrum can drift a few channels even during a short, e.g., few minutes, acquisition period smearing out the signal. The spectral alignment strategy here is based on the premise that all spectra, acquired in a short period sequentially from the same specimen under the same experimental conditions, are correlated except for an energy drift. Once a particular feature is aligned, all the features on the spectra are aligned simultaneously.

(3) Monitoring the Change in Thickness: Both the background and the fine structure of a spectrum may change with time due to both sample and beam drifts during long acquisitions, e.g., tens of minutes to few hours. Thickness variation is monitored in real time and readjustment of the sample is made as required.

(4) Monitoring Variations of Energy Resolution: The energy resolution of the EELS spectrometer may change during a long acquisition due to instabilities. Worsened energy resolution manifests itself in smeared features. To

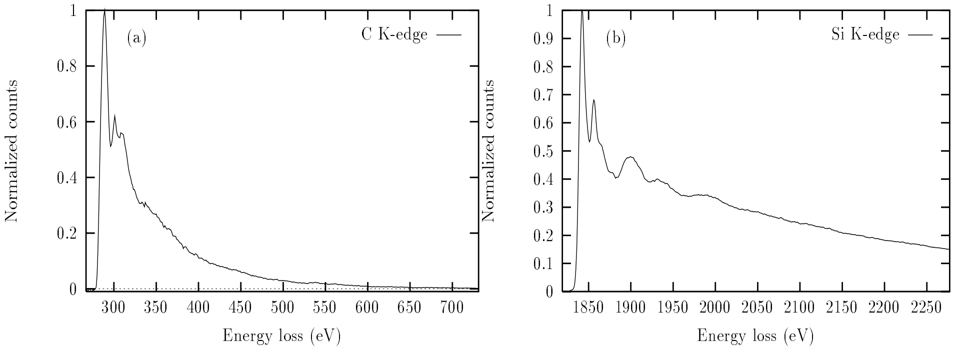

Figure 1: (a) C and (b) Si K-edge EEL data after sharpening, pre-edge removal, and plural scattering correction.

monitor this effect, the AcqLong program is instructed to quantify a chosen sharp feature and post a warning message if there is a significant change. One can then temporally stop the acquisition and take pertinent action.

(5) A Flexible Way to Correct Dark Current: The dark current of a detector is temperature dependent, changing quite rapidly at the beginning of an experiment and taking 1 or 2 hrs. to stabilize, necessitating frequent on-line calibration. This is done by taking a dark-current spectrum just before starting AcqLong with the set-up conditions to be used in the experiment and making the program automatically subtract this dark-current from each read-out.

(6) Monitoring Radiation Damage: Radiation damage is a complex phenomenon and, hence, it is impossible to determine the details about the damage on-line. In most cases, only the detection of the beginning of radiation damage is necessary.[12] The damage can be monitored by measuring a radiation-sensitive near-edge feature for each individual read-out for pronounced changes, for which the AcqLong program gives a warning message, requiring to stop the acquisition and moving to a new region.

(7) EXELFS Analysis Software: In addition to the lack of statistically significant spectral acquisition, the absence of a proper EXELFS analysis software has been a major drawback. A sophisticated XAFS data analysis software, i.e., UWXAFS, has already been developed and allows to accurately determine structure out to fourth nearest neighbors and further.[13] Since the fundamentals behind EXELFS and XAFS are the same, we have adapted the UWXAFS analysis software to EXELFS.[11] For this, however, spectral processing needs to be done before extracting the c-data, which should exactly be equivalent to the XAFS one. The differences between EXELFS and EXAFS include spectrometer energy resolution, plural scattering due to plasmon excitation, and energy dependence of pre-edge and post-edge background. We have developed the spectra acquisition and EXELFS analysis software, based on XAFS, incorporating all the developments discussed above. [8-10] Another problem, namely, separation of overlapping edges, has also been dealt with. In EXELFS, the energy edges are often narrowly spaced and the workable extended energy range without overlapping is, in many cases, only about 200 eV. It is necessary then to correctly separate these edges for maximum EXELFS information . Currently, this problem is being addressed. [11]

3 Applications

The improved EXELFS technique described has been applied to the analysis of a variety of complex materials.[8-10,14] To illustrate the technique we present results on SiC. C and Si-K edge EXELFS were measured at 200 keV with a Phillips 430T TEM in the diffraction mode. Camera length of 250 mm and a spectrometer entrance aperture of 3 mm were used. The inelastic scattering cross-section is much larger at the C-K edge (284 eV) requiring about 10-15 minutes to accumulate 106 counts while about 1 hour is required at the Si-K edge (1,839 eV). The electron current was set to 12 nAmps. and the radius of the electron probe to 0.5 mm.

Figures 1 (a-b) show the respective EEL spectra after sharpening by deconvoluting with the zero loss peak, pre-edge removal and plural scattering corrections due to plasmon excitations. The thickness of our sample was about 0.3 λ, with λ being the 200 keV electron mean-free- path. The post-edge background was defined by those frequencies for which $r \leq 1\,\text{Å}$ and the EXELFS was subtracted by normalizing by the energy dependent background. [15] Our experimental set-up guarantes collection of dipole-scattered electrons only and, hence, XAFS theory can be used as our standard. FEFF6 calculation [16] was done on the known crystal structure. [17] The fitting was done in r-space simultaneously for both edges since the first shell distance and thermal disorder is the same irrespective of the central atom. This reduces the number of parameters needed.

The $r = (1.2 - 2.0)\,\text{Å}$ (first shell) and $k = (2, 7)\,\text{Å}^{-1}$ regions were used to fit the C data, while $r = (1.2, 3.0)\,\text{Å}$ (first and second shells) and $k = (2.5, 9.50\,\text{Å}^{-1}$ regions were used for the Si fit. Note that we start fitting at 1.2 to avoid the background region. Figures 2 (c-d) show the fit results. The following parameters were obtained: $S_0^2 = 0.8(1)$, $0.9(1)$ for C and Si respectively; $\delta r = -0.0003 \pm 0.15\,\text{Å}$ and $\sigma^2 = 0.0015 \pm 0.0013\text{Å}^2$ for Si-C bonds; $\sigma^2 = 0.008 \pm 0.002\,\text{Å}^2$ for Si-Si bonds. The Si-Si distance was related to the Si-C one by the Zincblende structure. Coordination numbers were set as in the known structure. In addition, an overall E_0 shift was varied for each edge. In short, excellent agreement

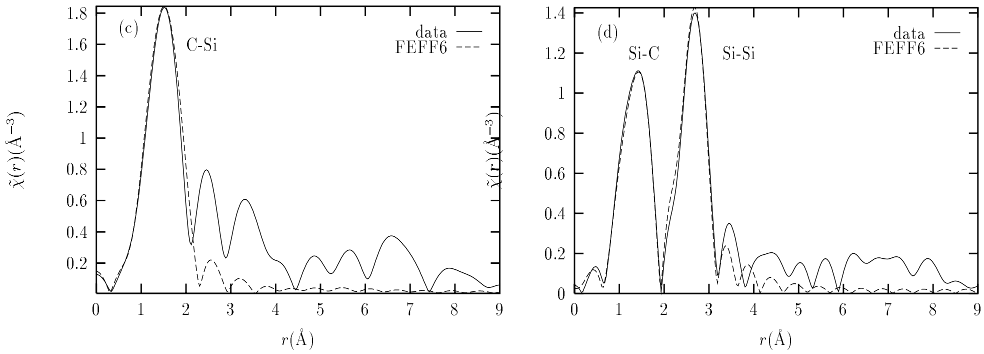

Figure 2: Magnitude of complex Fourier transformed EXELFS for (c) C-K edge and (d) Si-K edge. Fit results of theory (dotted line) to data are also shown.

with the known structure was obtained, giving confidence to our data collection and analysis procedures.

4 Summary, concluding remarks and future prospects

The use of EXELFS is discussed and compared to XAFS. The problems hitherto associated with EXELFS have been listed and their solution described in the newly developed AcqLong program.[11] The implementation of improved acquisition and data analysis procedures were demonstrated in the quantitative structure analysis of SiC. The improvements in the EELS acquisition program [8-10,14] coupled with the benefits of parallel detection [7] and the adaptation of advanced XAFS programs to the EXELFS analysis [11], make the quality of EXELFS data now comparable to that obtained at a synchrotron source. In addition, EXELFS experiments can be performed in one's laboratory (avoiding a clearly inconvenient trip to a synchrotron source) at high spatial resolution, typically 50 nm limited by radiation damage. The same sample region can be further investigated by high spatial resolution TEM techniques.

The EXELFS can be a routine technique on every TEM that is properly equipped with a parallel EEL detector for analysis of a wide variety of inhomogeneous, complex, multiphase, and nanostructural materials. Further developments in lattice site specific [18] and orientation resolved [19] EXELFS, in deconvolution of overlapping edges, use and cross-correlation of mixed edges (K, L, M) in the presence of two or more elements, are all important for wider future applications of the EXELFS spectroscopy.

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