

Enabling electron-energy-loss spectroscopy at very high energy losses: An opportunity to obtain x-ray absorption spectroscopy–like information using an electron microscope

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Electron-energy-loss spectroscopy (EELS) with an electron microscope and X-ray absorption spectroscopy (XAS) with a synchrotron are techniques for material characterization, both of which are based on exciting core electrons. Both techniques have a similar energy resolution, but while the spatial resolution of EELS can drop to atomic scales, the spatial resolution of XAS is typically limited to micrometer scales. Yet, XAS is commonly the preferred technique for analysis of the extended fine structure of ionization edges, mainly thanks to the excellent signal-to-noise ratio and the large range of ionization energies (from ~ 5 to ~ 40 keV) that can be probed at synchrotron end stations. In contrast, EELS is traditionally limited to ionization energies of $\lesssim 2$ keV because electrons in the beam that lose more than 2 keV will be too distant from the operating energy of the electron microscope. Chromatic effects in the postsample lenses allow only some of such energy-loss electrons to reach the EELS detector, as the latter electrons will either suffer from being strongly defocused or will not make it to the detector at all. In this paper, we present results from our novel Iliad EELS spectrometer, which offers a greatly increased range of ionization energies up to 30 keV. We achieve this vast increase by carefully controlling the optics of our electron microscope and carefully matching the optics of our EELS spectrometer to it, such that all the chromatic effects are removed or compensated. We exemplify its performance by recording EELS near-edge fine structure (ELNES) of the Zr L-edges at 2.3 keV, extended fine structure EELS (EXELFS) of Cu K-edge at ~ 9 keV, and EELS of the Mo K-edge at 20 keV and Sb K-edge at ~ 30 keV. We benchmark our data against near-edge and extended fine structure X-ray absorption (XANES and EXAFS) data, and we quantitatively analyze the Cu K-edge EXELFS, demonstrating the capability to determine element-specific bond lengths and to distinguish different oxidation states such as metallic Cu, Cu₂O, or CuO on a submicrometer scale.

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I. INTRODUCTION

Electron-energy-loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS) are techniques for material characterization, both of which probe the bonding energies of core electrons. An incoming electron or an incoming

X-ray interacts with a core electron in the sample, transfers energy to this electron, and excites it to an unoccupied state. Depending on the amount of energy transferred, the excited electron can occupy one of the higher unoccupied orbitals or a delocalized state with very low kinetic energy, thus giving rise to the near-edge fine structure in the spectrum (known as ELNES and XANES, typically up to a few tens of electronvolts after the onset of the edge), or the electron can escape the atom with high excess energy (kinetic energy) and travel to and interfere with neighboring atoms, thus, giving rise to the extended fine structure in the spectrum (known as EXELFS and EXAFS, typically up to several hundreds of electronvolts after the onset of the edge). Thus, ELNES and XANES can be

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used to obtain information about the oxidation state, local coordination environment, and electronic structure, and EXELFS and EXAFS can be used to extract quantitative and element-specific information on average bond length, coordination number, and species of neighboring atoms.

Modern XAS was introduced by Sayers, Stern, and Lytle in 1971 [1], following which it has evolved into a powerful technique applied across physics, material science, chemistry, geology, and environmental science, as well as art conservation and archaeology [2]. XAS is usually performed at synchrotron radiation facilities, which provide intense and tunable X-ray beams and commonly can probe XAS at ionization edges within an energy range from 5 to 40 keV. For energies lower than 5 keV, a dedicated soft X-ray beamline is usually needed. XAS has the advantage over EELS that a very large energy range can be probed with a very good signal-to-noise ratio, but its micrometer-scale resolution is typically not sufficient to individually probe different phases in heterogeneous materials on the submicrometer scale.

EELS is usually performed in (scanning) transmission electron microscopes (S/TEM). These instruments enable spatial resolution at the atomic level, which facilitates research on, e.g., nanomaterials, nanodevices, catalysts, and batteries. So far, the performance of EELS above about 2 keV energy loss is often insufficient with respect to signal intensity and energy resolution to perform ELNES. Being limited to losses between 0 and 2 keV in the past, EXELFS now enables harvesting bonding or coordination state information at a high spatial resolution, which was hardly attainable with the S/TEM since, beyond the ionization edge for a range of hundreds of electronvolts, the oscillations have to be measured and analyzed. The latter range, where the extended fine structure lies, can be easily affected by the presence of other edges from different elements present in the materials when the measurement data are acquired in the first couple of kilovolts of energy loss. Moreover, especially when the element of interest is diluted in the atomic percentage range, the signal strength of EELS can fail to provide this type of information at such high energy losses.

The decrease in signal strength and energy resolution of EELS above 2 keV is caused by several factors. The primary cause is that the energy of the energy-loss electrons no longer matches the operating energy of the electron microscope. This causes large chromatic effects in the magnetic lenses downstream of the sample, which means that these energy-loss electrons will reach the EELS detector either strongly defocused or not at all, except for a few energy-loss electrons that happen to exit the sample precisely on the optical axis of the microscope. A second cause is that, due to the decreased cross-section for high energy loss, the intensity of the energy-loss electrons is several orders of magnitude weaker than the intensity of the zero-loss electrons.

Thus, to the microscope's operator, the energy-loss electrons are completely obscured by the intense zero-loss beam, and it is impossible to visually assess whether the energy-loss electrons have been properly guided to the entrance aperture of the EELS spectrometer. Furthermore, the weak intensity often makes it practically impossible for the operator to manually refocus the EELS spectrum by examining the width of a high-energy EELS edge. Finally, because of the conservation of momentum, energy-loss electrons are scattered to increasingly larger angles at increasingly larger energy loss, making it increasingly challenging to collimate and transfer them to the EELS spectrometer.

Manual adjustment of the postsample lenses of the electron microscope, based on trial-and-error and/or computer simulations [3–6], can boost the EELS signal to a level that an EXELFS analysis becomes possible up to 12 keV [6], but still with suboptimal efficiency for collection of the energy-loss electrons, considering the long exposure times and high electron doses reported in Ref. [6].

In this paper, we present novel results from our new Iliad EELS spectrometer. When we developed this spectrometer, one of our aims was to increase (as much as possible) the range of ionization energies that this spectrometer could properly record with optimal resolution and optimal signal strength. To this end, we analyzed the chromatic defocus effects that can occur in the post-sample lenses of our electron microscope, we developed lens settings that minimize these chromatic effects, and we developed automated calibration and correction routines to correct the remaining chromatic defocus using the optics of the spectrometer. All these improvements led to the development of the extreme EELS (XEELS™) capability, which extends the range of EELS from ~ 2 to ~ 30 keV.

We exemplify this with a number of experiments where we compare and benchmark our EELS data with XAS data. We show the ELNES data of Zr L-edges at 2.3 keV in zirconium-rich precipitates in magnesium-alumosilicate (MAS) glass ceramics with energy resolution that extends far beyond earlier attempts in the literature [3,4,7]. We record EXELFS data of the Cu K-edge at ~ 9 keV in Cu, CuO, and Cu₂O, and we quantitatively analyze these data to determine the element-specific bond lengths and to evaluate whether these phases could, thus, be distinguished in an unknown sample. Finally, we explore the limits of our spectrometer by recording the Mo K-edge at 20 keV and Sb K-edge at ~ 30 keV for elemental Mo and Sb, respectively.

II. EXPERIMENTAL

The EELS experiments were performed on an Iliad Ultra scanning transmission electron microscope operating at a beam potential of 300 kV, equipped with an Ultra EDX detector and Iliad EELS spectrometer. Spectra were recorded on the Zebra EELS detector, which has

five independently readable indirect (i.e., scintillator) one-dimensional sensors, each consisting of 2048 pixels of $14\ \mu\text{m} \times 800\ \mu\text{m}$. A digital twin of the microscope's optics, downstream of the sample, was created in order to analyze and quantify its chromatic effects up to a third order. Combinations of lens settings that showed excessive third-order chromatic effects in the digital twin were replaced by combinations with reduced effects. The resulting effects were checked and calibrated against refocusing elements (several magnetic multipoles and one electrostatic quadrupole) in the spectrometer using automated calibration routines that stepwise apply offsets to the microscope's operating voltage. Next, with each change of the microscope optics (e.g., to change the collection angle) or of the spectrometer optics (e.g., to change dispersion or to shift the spectrum to a specific energy range of interest), the calibrated refocusing elements are automatically applied to ensure that

the EELS spectra remain in focus. After these initial calibrations, the microscope and spectrometer are set to the proper acquisition conditions, the sample is inserted, and one final tuning of the energy resolution at the zero-loss peak is undertaken. In our present setup, we calibrate the energy scale by offsetting the microscope's high-tension supply. Since this supply has an absolute accuracy of about $\lesssim 0.1\%$, our present setup has an absolute accuracy of, e.g., about $\lesssim 10\ \text{eV}$ at a 10 keV loss. Of course, this absolute accuracy can be improved by calibrating our energy scale against core-loss spectra of well-known energy. We expect that such a calibration can improve the absolute accuracy to well below 2 eV at a 10 keV loss. The energy stability of the system is about 1 eV per 8 h.

All the experiments were performed in STEM mode by acquiring a spectrum image (SI) dataset from a region of

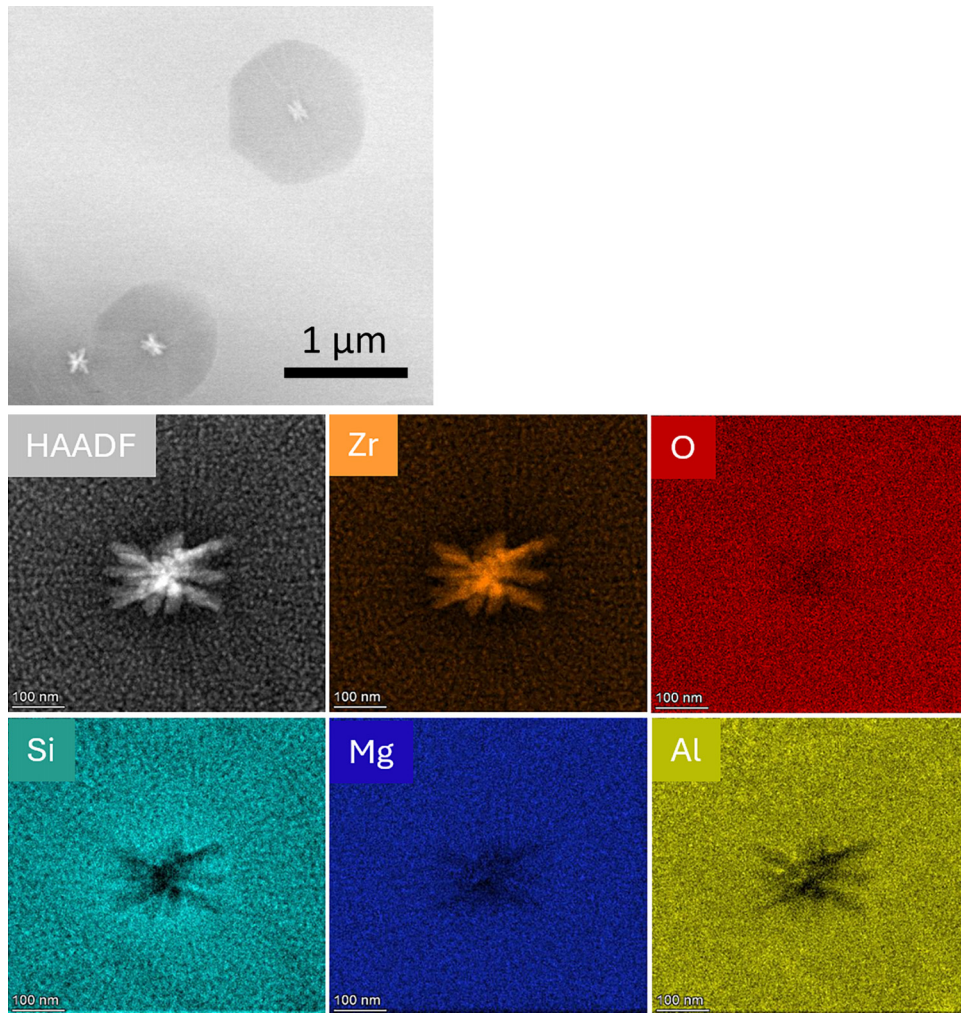


FIG. 1. (upper) Low-resolution STEM image of the sample at $t = 30\ \text{min}$: high-quartz solid solution domains are embedded within a still-amorphous MAS matrix. (lower) High-resolution STEM and EDX maps of a star-shaped ZrO_2 dendrite in the middle of a high-quartz solid solution crystal domain, in which spherical ZrO_2 nanocrystals are embedded.

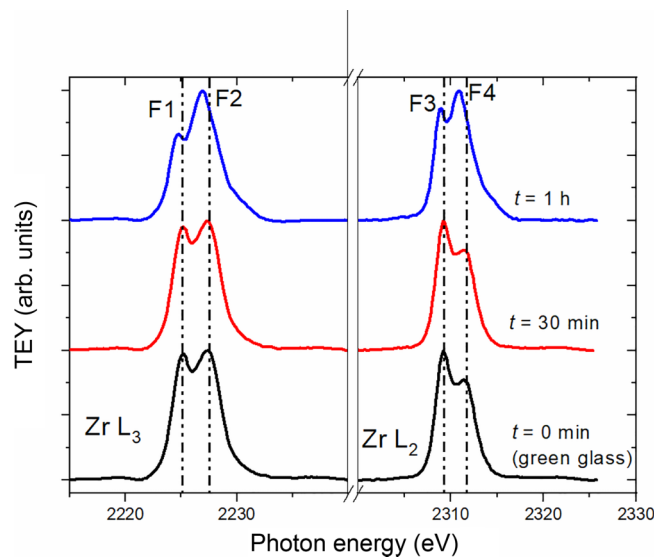


FIG. 2. XANES spectra recorded at the Canadian Light Source using the Soft X-ray Micro Characterization Beamline. From the lower to upper panel, the crystallization of high-quartz solid solution, accompanied by ZrO_2 crystallization, proceeds with an ongoing annealing time. In the base glass sample, CN=6. At $t = 1$ h, the fine structures F1, F2, F3, and F4 have changed significantly, indicating a shift from CN=6 to CN=8 in the bulk. For more details, see Ref. [10].

interest. The experimental conditions for each particular experiment are described.

III. Zr L-EDGE ELNES OF ZrO_2 PRECIPITATES IN GLASS CERAMIC MATERIAL

As a first test, we studied a sample of the magnesium-alumosilicate (MAS) glass-ceramic system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$ [8–10]. The sample was created and prepared as described in Ref. [10]. When annealed at 950°C , this

system crystallizes from base glass to a glass ceramic consisting of domains of high-quartz solid solution, which is a hexagonal quartz polymorph that can be stabilized at temperatures below 573°C – the temperature above which pure SiO_2 can crystallize in a hexagonal (high-quartz) polymorph. With the incorporation of a certain amount of MgO and Al_2O_3 , the high-quartz phase can be stabilized at lower temperatures. We are interested in the ZrO_2 precipitates that act as nucleation agents in this crystallization. Specifically, we want to track when and where the Zr changes from its initial sixfold coordination in the base glass to its final eightfold coordination in the ZrO_2 crystals in the glass ceramic.

References [8,10] showed that this crystallization starts with the precipitation of star-shaped ZrO_2 nanocrystals of $\sim 100\text{--}200$ nm in size. The zones around these star-shaped crystals are depleted in Zr and are the sites from where the high-quartz solid solution starts to grow. Figure 1(a) shows such a sample after 30 min of annealing. The darker areas are the domains of the high-quartz solid solution, with the clearly recognizable star-shaped ZrO_2 nanocrystals in their centers. Figure 1(b) shows our STEM and EDX maps of such a star-shaped nanocrystal. The Zr map shows the high concentration of Zr in the star-shaped precipitate and the depletion of Zr in the zone surrounding it. The Zr map also shows myriads of dots of Zr outside this zone. These dots are secondary spherical ZrO_2 nanocrystals of ~ 10 nm, which are expelled as the high-quartz solid solution expands. After approximately 1–2 h of annealing, the crystallization is completed and the sample consists of micron-scaled domains of high-quartz solid solution, at the boundaries of which residual MAS glass pockets are left.

Thus, the star-shaped primary precipitates and secondary spherical precipitates of ZrO_2 play an important role in the crystallization of the glass ceramic and, thus, in its resulting properties such as hardness, Young's modulus, and strength. To fully understand the crystallization,

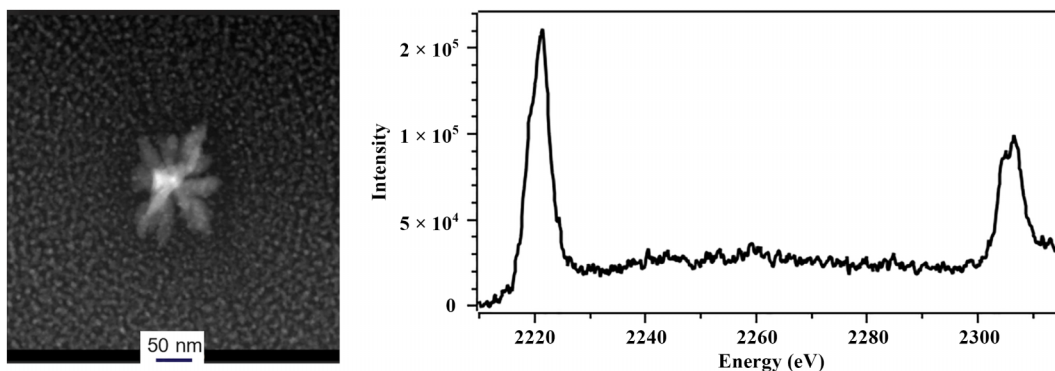


FIG. 3. (left) Zirconium-rich precipitates in the glass-ceramic system $\text{MgO-ZnO-Al}_2\text{O}_3\text{-SiO}_2\text{-ZrO}_2$. (right) EELS spectrum (background subtracted) taken from the center of this precipitate. Settings: Iliad Ultra operating at a beam potential of 300 kV, electron source monochromated to an energy spread of 170 meV, a probe current of 500 pA, a cumulative acquisition time of 4 min, a dispersion of 0.17 eV/pixel, and an EELS semi-acceptance angle of 25 mrad.

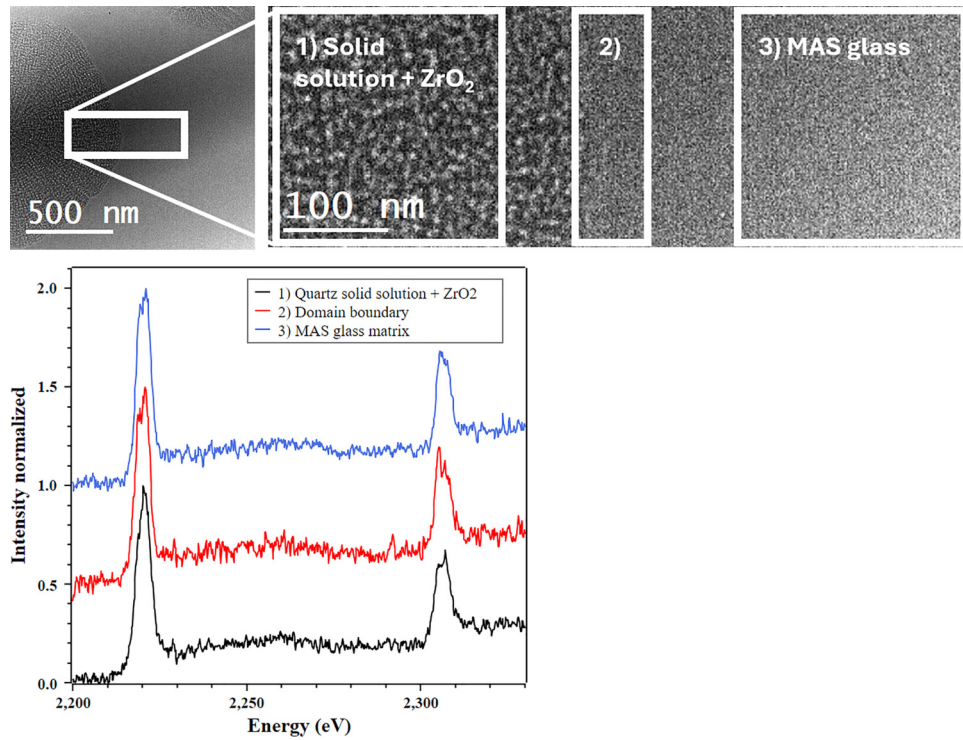


FIG. 4. (upper) HAADF micrograph of a $t = 30$ min annealed MAS glass sample that shows high-quartz solid solution crystal domains within the amorphous MAS glass matrix (left). Magnified inset (right) area at the domain boundary crystalline-amorphous, with the three subareas used for Zr $L_{2,3}$ ELNES with high spatial resolution. (lower) Zr $L_{2,3}$ ELNES spectra of the three different areas showing different distinct features of the edges that can be attributed to local differences in the coordination number of Zr (background subtracted). Settings: Iliad Ultra operating at a beam potential of 300 kV, electron source monochromated to an energy spread of 170 meV, a probe current of 500 pA, and an integration time of about 5 min for (1) and (3), and 2 min for (2), a dispersion of 0.17 eV/pixel, and an EELS semi-acceptance angle of 25 mrad.

it is important to understand when and where the ZrO_2 dissolved in the base glass transitions to ZrO_2 precipitates.

ZrO_2 has different polymorphs [11–13]: monoclinic (m- ZrO_2 , coordination number CN = 7), which is the stable phase at room temperature, and cubic (c- ZrO_2 , CN = 8) and tetragonal (t- ZrO_2 , CN = 8) phases that exist at high temperatures, which can be preserved at room temperature via size stabilization. Zr may also be incorporated in other oxide phases, such as $ZrTiO_4$, which has CN = 6. Figure 2 shows the XANES spectra of the MAS glass after various times of annealing. By comparing the fine structure in the Zr $L_{2,3}$ -edges with reference XANES spectra [10], it can be concluded that, somewhere between 30 min and 1 h of annealing, the ZrO_2 transitions from predominantly CN = 6 to predominantly CN = 8, in accordance with the formation of the ZrO_2 nanocrystals. However, the $\sim 1 \mu m$ resolution of XANES is insufficient to assess the coordination numbers of the star-shaped ZrO_2 nanocrystals or the spherical ZrO_2 nanocrystals separately. In particular, XANES cannot track the coordination numbers of the nanocrystals in the initial stage of the annealing, e.g., after ~ 30 min, where the first nanocrystals have already formed, but the majority of Zr is still preserved in the amorphous

glass matrix, leading to a domination of the Zr-L XANES signal of the Zr with CN = 6 within the bulk glass.

The much better spatial resolution of ELNES can help to track the coordination number of the emerging nanocrystals, provided the EELS spectrometer has sufficient energy resolution and collects a sufficient signal to reveal the fine structure in the Zr $L_{2,3}$ -edges. Thus, as a first test of our new EELS spectrometer, we recorded ELNES spectra on a sample MAS glass that had been annealed for 30 min.

Figure 3 shows an EELS spectrum recorded from a star-shaped nanocrystal in the center of a high-quartz solid solution domain. In contrast to earlier reported Zr $L_{2,3}$ -edge spectra [4], our ELNES spectrum clearly reveals the fine structures F1, F2, F3, and F2 (cf. Fig. 2), indicating that the local coordination number of Zr is CN = 8 at this specific position. We consider the quality of this ELNES data to be remarkably good.

Figure 4 shows the EELS spectra of three areas across the boundary of a domain of high-quartz solid solution. Area 1 is within the domain and has the spherical ZrO_2 nanocrystals embedded in it, area 2 covers the domain boundary, and area 3 is within the still-amorphous MAS glass matrix. Clearly, it can be seen that the Zr is eightfold

coordinated within the high-quartz solid solution crystal domain (area 1), indicating that the nanocrystals seen with TEM and STEM are either t- or c- ZrO_2 . Also, within the MAS glass matrix (area 3), the features of the Zr $L_{2,3}$ ELNES spectrum are in accordance with the XANES results of the MAS base glass sample ($t=0$ min, cf. Fig. 2) – i.e., within the residual glass matrix in the samples after $t=30$ min annealing time, it is obvious that the Zr is still sixfold coordinated. Additionally, a “transition zone” (area 2) between crystal and amorphous glass matrix was analyzed with ELNES. The results, as shown in Fig. 4, indicate neither a clear spectral shape of CN = 6 or CN = 8 but rather a mixture between the two.

Thus, with the high-energy-loss EELS approach, the possibility of gaining spectral data that is similar to the XAS spectral data is shown. Although the ELNES data is noisier than the XANES data, the substructure of the L-edges is still clearly visible and quantifiable, thus enabling a similar assessment of the local coordination of zirconium but with an additional surplus of unprecedented spatial resolution.

IV. BENCHMARKING EELS VERSUS XAS USING THE Cu K-edge

A. Metallic copper

As a subsequent test, we study the Cu K-edge at 8979 eV. This edge is often used at synchrotrons to benchmark XAS beamlines, so it also represents a good benchmark for our EELS performance. We used a FIB-prepared copper lamella and the data was acquired from an area with a thickness of 50 nm. Figure 5 shows a spectrum image (SI) scan over 30×30 pixels, together with the resulting Cu K-edge EELS spectrum when summing over 30, 90, or all 900 pixels. The decreasing noise with the increasing number of pixels is clearly apparent.

We process our EELS spectra using the ATHENA software [14,15], which is standard software used in the XAS community. The first steps in this processing are background subtraction, normalization, and flattening [2]. Figure 6 compares the, thus, processed 900-s EELS data (blue curve) with the XAS data of a 10- μm -thick Cu foil (gray curve). The extended fine structure of our EELS data exhibits the same qualitative features as the XAS data, but the EELS data shows a lower intensity in the ELNES region and up to ~ 120 eV above the Cu K-edge. Further measurements showed that this intensity difference close to the edge does not noticeably depend on the collection angle of the EELS spectrometer, but it does grow with increasing specimen thickness. This indicates that it must originate from multiple inelastic scattering of the electron beam with plasmons; such a plasmon interaction is stronger for electrons than for X-rays. Indeed, as shown in Fig. 6 (orange curve), when we deconvolve the EELS

data with the low-loss EELS spectrum (up to 100 eV), this intensity difference disappears. This illustrates the importance of being able to record EELS spectra at core-loss and low-loss for the same area.

The fine structure oscillations in the EELS data have a smaller amplitude than the XAS data, especially in the first ~ 50 eV above the edge. We attribute this to the slightly worse energy resolution of the EELS data, which is related to the broadening by the modulation transfer function of the EELS sensor and due to the intrinsic energy width of the electron source. Further analysis of the ELNES data is, therefore, not reasonable but the strong similarity between EXELFS and EXAFS (see Fig. 6) warrants a quantitative analysis of the extended fine structure as it is typically undertaken for synchrotron data [2].

To this end, the energy-dependent fine structure $\chi(E)$ is transformed into the wave-number-dependent fine structure $\chi(k)$ and a weighting factor k^2 is applied to boost the signal at high k . These data are then Fourier transformed into radial space and the resulting $\chi(R)$ is used to visualize and analyze the scattering contributions from different coordination shells. For a meaningful comparison, we process the data in the ATHENA software using the same set of parameters for the EELS and the XAS datasets. Figure 7 plots the resulting extended fine structures $k^2\chi(k)$ and the magnitude of the Fourier transformations $|\chi(R)|$. Apart from the somewhat reduced amplitudes, the EXELFS data show very good agreement with the EXAFS data for $k^2\chi(k)$ up to $10 \text{ \AA}^{-1}$. The excellent match of the zero-crossings, in particular, indicates an almost identical frequency spectrum. This is confirmed by the $|\chi(R)|$ data, which exhibits the same peaks at basically the same R values only with reduced amplitude for the EXELFS compared with the EXAFS. Note that the deconvolution of the EXELFS data with the low-loss EELS spectrum (which effectively shifts the intensity from the inelastic plasmon scattering back to the zero-loss peak) significantly increases the amplitude for both $k^2\chi(k)$ and $|\chi(R)|$, bringing them closer to those of the EXAFS data. We attribute the remaining difference to the slightly worse energy resolution of the EELS data.

It is worth mentioning that these EXELFS results are effectively resilient against the low signal. Figure 8 presents the same analysis using 10 or 30 times less dose compared with Fig. 7. The reduced dose still provides a surprisingly similar indication of the bond length based on $|\chi(R)|$, although the increased noise of the data is readily apparent for the $k^2\chi(k)$ data, especially for the 30-s spectrum. Such resilience is typical for analyses that quantify the lowest Fourier components in a weak signal.

The bond length can be determined using a path-fitting approach [2] and ARTEMIS software [14,15]. Here, we fit the nearest neighbor scattering contribution in radial space over a range of $R = 1.4\text{--}2.9 \text{ \AA}$, applying multiple k -weights of 2 and 3. Phase shifts and scattering amplitudes are

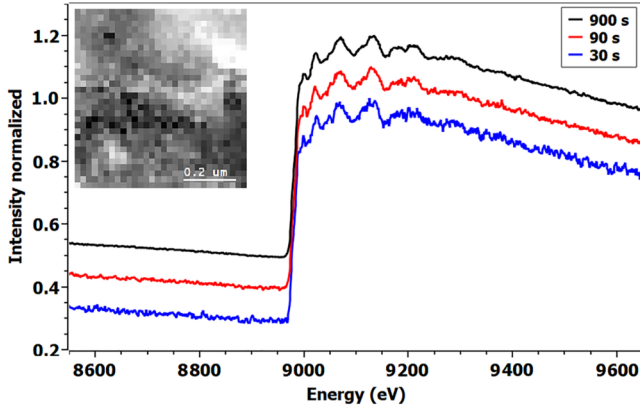


FIG. 5. Inset: 30×30 spectrum image (SI) scan map of metallic copper. EELS spectra (unprocessed) created by summing spectra from 30, 90, and 900 pixels of the SI, representing cumulative acquisition times of 30 s, 90 s, and 900 s, respectively (corresponding to doses of $1.8 \times 10^{12} \text{ e}^-$, $5.6 \times 10^{12} \text{ e}^-$, and $5.6 \times 10^{13} \text{ e}^-$). Settings: Iliad Ultra operating at a beam potential of 300 kV, a probe current of 10 nA, acquisition time per pixel of 1 s, a dispersion of 0.97 eV/pixel, a probe semiconvergence angle of 21 mrad, and an EELS semi-acceptance angle of 34 mrad.

calculated using FEFF9 [17] based on the crystal structure of metallic Cu [18]. The threshold energy, the amplitude reduction factor, the bond length, and the EXAFS Debye-Waller factor are treated as free-fitting parameters. The fits are shown in the insets of Figs. 7 and 8 and the resulting bond lengths are listed in Table I. The 900-s dataset yields bond lengths that are in excellent agreement with the literature, whether it is low-loss deconvolved or not. The 10-times reduced dose of the 90-s dataset still results in a bond length that is only slightly too low by $\sim 0.03 \text{ \AA}$, corresponding to a difference of roughly 1%. The accuracy of the bond length obtained is, thus, determined mostly by the statistics (noise) of the data and not very much by

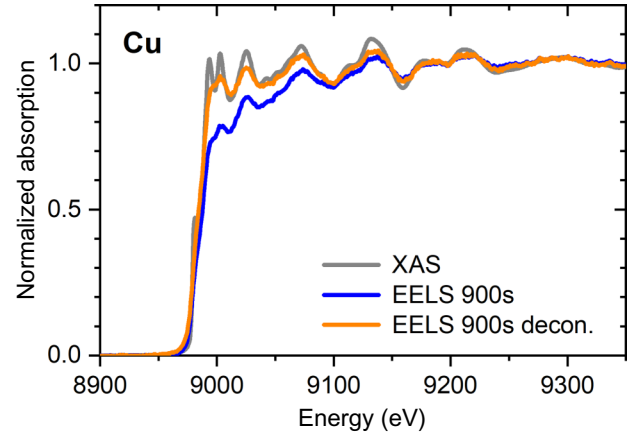


FIG. 6. EELS (900 s, without and with low-loss deconvolution) and the XAS data measured for metallic Cu at the Cu K-edge after background subtraction, normalization, and flattening. The XAS data was acquired at the beamline P65 [16] of PETRA III at DESY, using a Si 111 double crystal monochromator and a beam spot size of $0.3 \times 1.5 \text{ mm}^2$. The spectrum was recorded in continuous-scanning transmission mode at room temperature with a measurement time of 300 s.

the deconvolution. However, even the comparatively noisy 90-s data yields an astoundingly good quantitative value.

B. Copper oxides

Next, we turn to the copper oxides CuO and Cu₂O to investigate how effective our EXELFS capability can distinguish the difference in bond lengths between Cu, CuO, and Cu₂O. It is more challenging to record high quality EXELFS data from these copper oxides due to their increased susceptibility to radiation damage by the electron beam and due to the lower concentration of the copper. Radiation damage can be mitigated by lowering the acceleration voltage, cooling, or increasing the

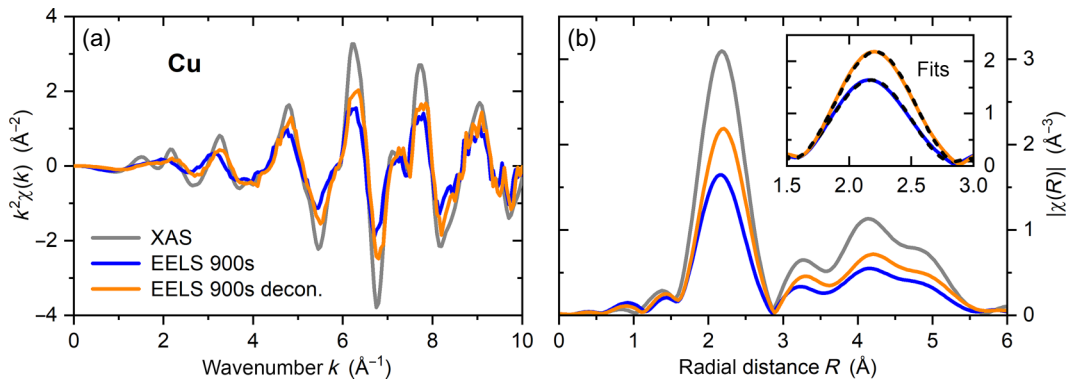


FIG. 7. (a) Extended fine structure $k^2\chi(k)$ as a function of wave number k and (b) magnitude of the Fourier transformations $|\chi(R)|$ as a function of radial distance R for the EELS (900 s, without and with low-loss deconvolution) and XAS data shown in Fig. 6. The Fourier transformation is performed using a Hanning window with $k = 3\text{--}10 \text{ \AA}^{-1}$ and a tapering parameter $dk = 2 \text{ \AA}^{-1}$. The inset shows the fit of the EELS data using the structural model.

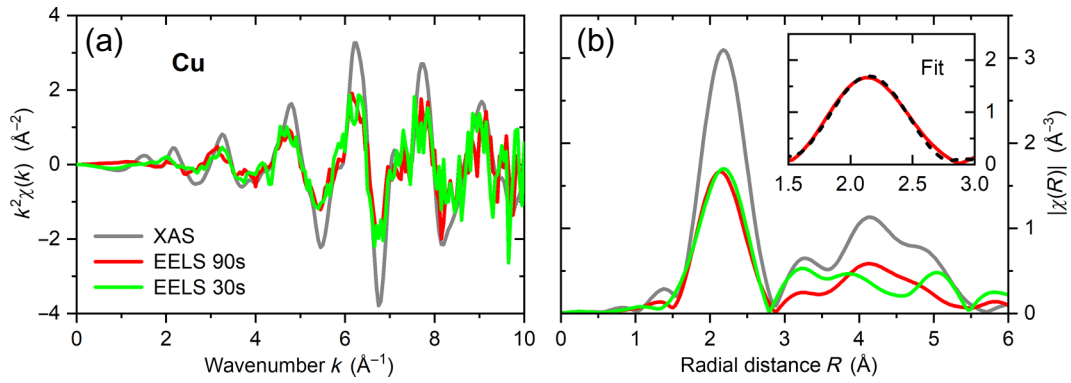


FIG. 8. (a) Extended fine structure $k^2\chi(k)$ as a function of wave number k and (b) magnitude of the Fourier transformations $|\chi(R)|$ as a function of radial distance R for EELS data acquired using 1/10 (90 s) and 1/30 (30 s) of the dose of the data from Fig. 7 (also compare with Fig. 5). The Fourier transformation is performed with the same settings as in Fig. 7 and the XAS data are shown again for a comparison. The inset shows the fit of the EELS data using the structural model.

probe size to reduce the current density at the sample, of course, impacting spatial resolution (angstroms to nanometers) but still considerably better than XAS. The samples were high-purity commercially available powders, which were dispersed in ethanol and drop-cast on a lacey carbon grid. The CuO and Cu₂O EELS data were recorded in a similar optical setup as the metallic Cu data, with the difference that they were acquired from nanoparticles and a region of interest between 100 and 200 nm in size. The results are shown in Fig. 9 together with the XAS data of graphite-diluted CuO or Cu₂O powder pellets with an effective thickness of 7 μm or 9 μm , respectively. Similar to the metallic Cu EELS data, plasmon scattering reduces the intensity in the ELNES region when compared with the XANES data. The extended fine structures $k^2\chi(k)$ show fair matches with the EXAFS data up to 8 $\text{\AA}^{-1}$ for both compounds, although the noise level is clearly higher compared with the EXELFS of metallic Cu. The magnitude of the Fourier transformations $|\chi(R)|$ also shows a good match with the EXAFS data in terms of overall shape and peak positions, whereas the amplitude is again strongly reduced for the EXELFS compared with the EXAFS.

TABLE I. Bond lengths resulting from a fitting analysis of the EXELFS datasets.

Bond length [$\text{\AA}$]	EXELFS analysis	Literature	
Cu (90 s)	2.529 ± 0.008	2.556	Ref. [18]
Cu (900 s)	2.545 ± 0.007		
Cu (900 s decon.)	2.553 ± 0.006		
Cu ₂ O	1.89 ± 0.06	1.85	Ref. [19]
CuO	1.95 ± 0.07	1.95 or 1.96	Ref. [20]
Mo R1	2.71 ± 0.02	2.725	Ref. [21]
Mo R2	3.11 ± 0.02	3.147	Ref. [21]

The differentiation of Cu₂O, CuO, and metallic Cu is not feasible with the current ELNES data (no deconvolution used), but it can be achieved based on the EXELFS data. For the distinction of metallic Cu and Cu oxides, a simple qualitative inspection of $|\chi(R)|$ is sufficient. For metallic Cu, the nearest neighbor Cu-Cu scattering peak is observed at ~ 2.2 $\text{\AA}$ while, for the Cu oxides, the nearest neighbor Cu-O scattering peak appears at ~ 1.4 $\text{\AA}$. In contrast, the distinction of the two different Cu oxides requires a quantitative fitting analysis, as described above. The phase shifts and scattering amplitudes are calculated based on the crystal structures of Cu₂O [19] and CuO [20] (also see Table I) and a fitting is performed over a radial range of $R = 0.8$ – 2.1 $\text{\AA}$. CuO features a split first coordination shell with two O atoms at 1.95 $\text{\AA}$ and two O atoms at 1.96 $\text{\AA}$ distance, a difference unable to be resolved even with the XAS data. Therefore, an average nearest neighbor bond length with a coordination number of CN = 4 is fitted. Apart from the bond length, the threshold energy and amplitude reduction factor are again treated as free-fitting parameters, while the EXAFS Debye-Waller factor has to be set to a fixed value. Note that the variations of this value, within a reasonable range, do not alter the bond length result. Each EXELFS dataset is now fitted twice, once with the model based on Cu₂O and once with the model based on CuO. The resulting bond length is the same in both cases and, therefore, does not depend on the details of the initial structural model, which is in perfect agreement with previous XAS studies [22].

The fits to the nearest neighbor scattering signal are shown in the insets of Figs. 9(e) and 9(f) and the corresponding bond lengths are given in Table I. For both Cu₂O and CuO, the results are in excellent agreement with the literature. Furthermore, the Cu₂O bond length is smaller than the CuO bond length. Although this difference is slightly smaller than the literature values and similar to

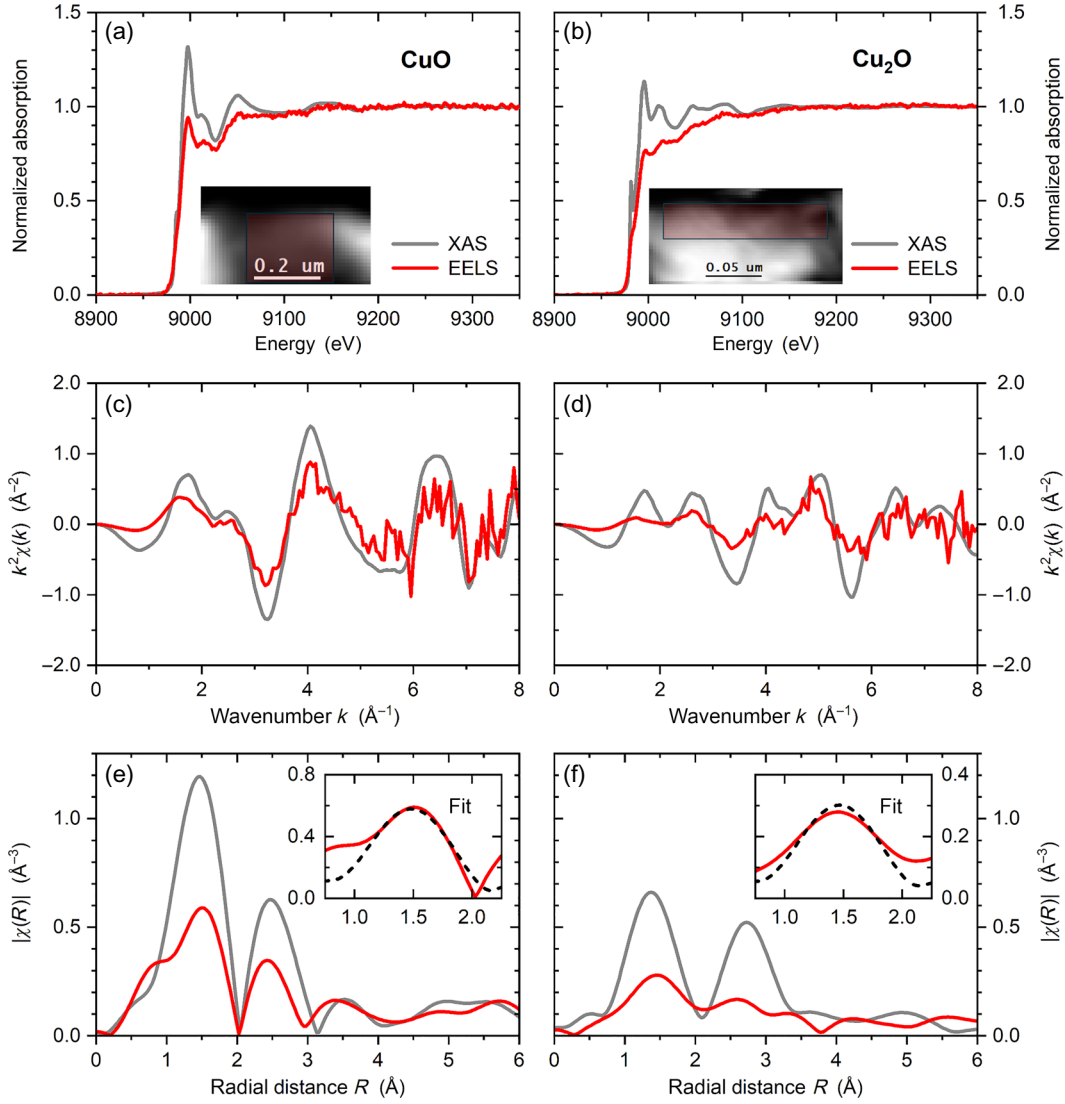


FIG. 9. (left) Comparison of the EELS and XAS data of CuO, (a) spectra after background subtraction, normalization, and flattening, SI image with ROI in the inset, (c) extended fine structure $k^2\chi(k)$, and (e) magnitude of the Fourier transformations $|\chi(R)|$. The inset shows the fitting of the EELS data using the structural model. The EELS spectrum was recorded with dose $\sim 1.6 \times 10^{13} \text{ e}^-$. (right) Comparison of the EELS and XAS data of Cu_2O , (b) spectra after background subtraction, normalization, and flattening, SI image with ROI in the inset, (d) extended fine structure $k^2\chi(k)$, and (f) magnitude of the Fourier transformations $|\chi(R)|$. The inset shows the fitting of the EELS data using the structural model. The EELS spectrum was recorded with a dose of $\sim 1.4 \times 10^{13} \text{ e}^-$. The XAS data was acquired at beamline P65 [16] of PETRA III at DESY, using the same experimental conditions as for the Cu foil in Fig. 6. The Fourier transformation is performed using a Hanning window with $k = 3\text{--}8 \text{ \AA}^{-1}$ and a tapering parameter $dk = 2 \text{ \AA}^{-1}$.

the uncertainty, it systematically persists and amounts to $0.06 \pm 0.01 \text{ \AA}$ for variation of all the fit settings within a reasonable range (i.e., Fourier transformation parameters, k -weights, fitting range, etc.). This shows that the present EXELFS capability can clearly differentiate these two compounds, even though the bond length difference is only as small as 6 pm.

V. EXTREME HIGH-ENERGY-LOSS EELS

In order to explore the maximum energy loss that can be properly studied in our EELS setup, we FIB-prepared

metallic molybdenum and antimony samples to record EELS data on the Mo K-edge at 20.0 keV and the Sb K-edge at 30.5 keV. Again, we compare our EELS spectra with XAS spectra [23,24], processing the data with ATHENA software and using the same set of parameters for both the EELS and the XAS datasets. Furthermore, the Mo EXELFS is fitted as described above, using calculated phase shifts and scattering amplitudes based on the crystal structure of metallic Mo [21]. The scattering contributions of the first and second nearest neighbors strongly overlap and are, therefore, fitted together using a radial range of

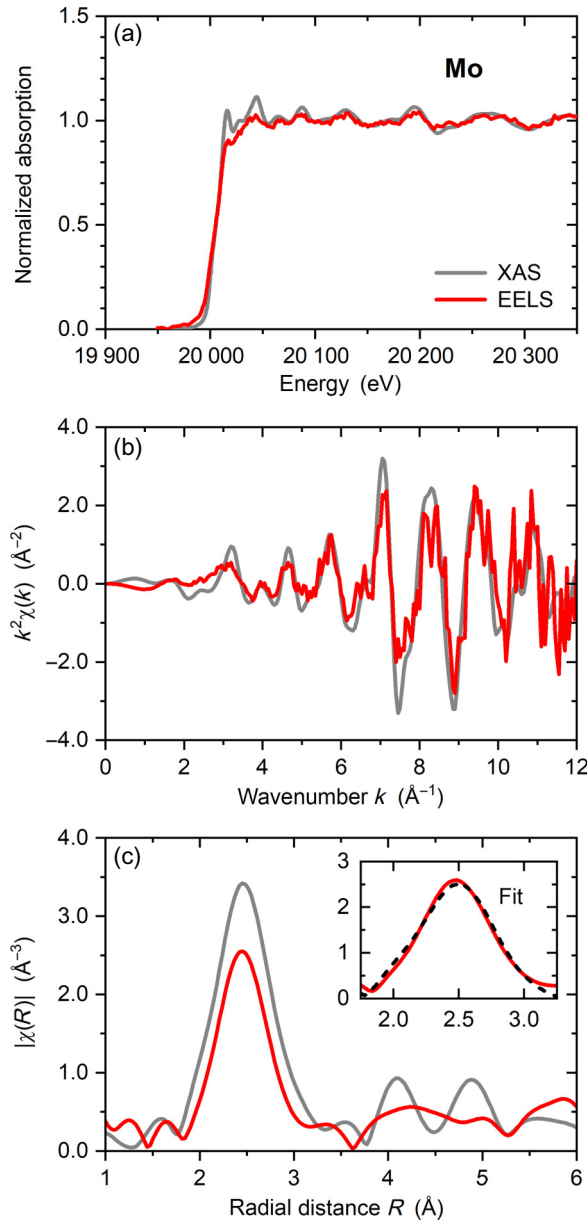


FIG. 10. Comparison of the EELS and XAS data of metallic molybdenum. (a) Spectra after low-loss deconvolution for EELS, background subtraction, normalization, and flattening, (b) extended fine structure $k^2\chi(k)$, and (c) magnitude of the Fourier transformation $|\chi(R)|$. FIB-prepared metallic molybdenum sample (thickness of about 45 nm). Settings: Iliad Ultra operating at 300 kV, probe current of 10 nA, SI image of 32×32 pixels at 0.5 s/pixel, a cumulative acquisition time of 512 s, an EELS semi-acceptance angle of 62 mrad. The XAS data is taken from Ref. [23]. The Fourier transformation is performed using a Hanning window with $k = 3\text{--}12 \text{ \AA}^{-1}$ and a tapering parameter $dk = 2 \text{ \AA}^{-1}$. The inset in (c) shows the fit of the EELS data using the structural model.

$R = 1.7\text{--}3.3 \text{ \AA}$ and multiple k -weights of 2 and 3. For each scattering path, the bond length and the EXAFS Debye-Waller factor are treated as free-fitting parameters, together

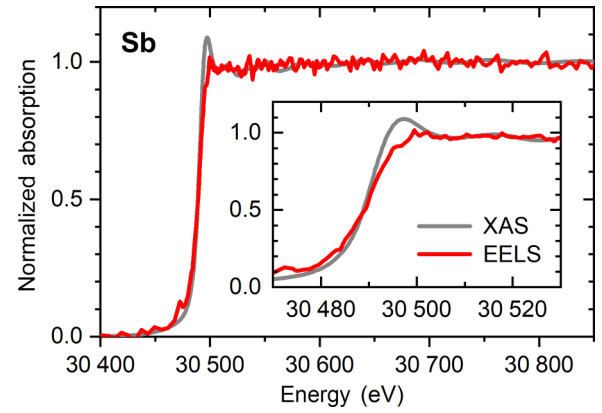


FIG. 11. Comparison of the EELS and XAS spectra (after low-loss deconvolution for EELS, background subtraction, normalization, and flattening) of metallic antimony. FIB-prepared metallic antimony sample (thickness of about 30 nm). Settings: Iliad Ultra operating at 300 kV, probe current of 20 nA, SI image of 23×17 pixels at 2 s/pixel, a cumulative acquisition time of 702 s, and an EELS semi-acceptance angle of 62 mrad. The XAS data is taken from Ref. [24].

with the threshold energy and the amplitude reduction factor that yields a total of six fitting parameters.

Figure 10 and Table I show the results for the Mo K-edge at 20.0 keV. The agreement between the deconvolved EELS spectrum and the XAS spectrum is good and the agreement between EXELFS and EXAFS is very good. Indeed, the magnitude of the Fourier-transformed EXELFS closely follows that of the XAS data with only a somewhat reduced amplitude and the resulting bond lengths R1 and R2 for the first and second nearest neighbors, respectively, are in close agreement with literature values.

Figure 11 shows the results for the Sb K-edge at 30.5 keV, indicating the current limitations of extreme high-energy-loss EELS. The energy resolution in this EELS spectrum is still very good, as demonstrated by the rise of the edge, which is as sharp in the EELS spectrum as in the XAS spectrum (see inset in Fig. 11). However, even though the probe current (20 nA) and the acquisition time (702 s) are very high, the signal-to-noise of the EELS spectrum appears to be too low to reproduce the near-edge fine structure or extended fine structure that the XAS spectrum exhibits. Further investigations are required by choosing other high-energy-loss edges to observe whether the limitation is related to this specific sample or material or whether it is intrinsic to the physics or the instrumentation.

VI. CONCLUDING REMARKS

When we developed our new Iliad EELS spectrometer, we exploited our understanding of the optics of the electron microscope's imaging system and especially of its chromatic effects to minimize and compensate for all

the chromatic effects by suitably adjusting the optics of the EELS spectrometer. As a result, we succeeded in extending the routinely available range of ionization energies in EELS from ~ 2 to 20 keV or more. With this extension, we bring a new range of analysis techniques to the electron microscope, which were previously only available at synchrotron facilities.

First, we illustrated this with a near-edge fine structure analysis of the Zr L-edges at 2.3 keV to successfully determine the coordination state of zirconium in precipitates a few tens of nanometers in size in a glass-ceramic system. The energy resolution of <2 eV at 2.3 keV, needed to distinguish between the different coordination states, was previously unattainable with EELS. The spatial resolution needed to isolate the Zr-spectra of the precipitates from the Zr-spectra of the bulk is unattainable at most synchrotron beamlines, but is readily available with the electron microscope.

The increase of the energy range in EELS to 20 keV is especially beneficial for extended fine structure analysis. The advantage of recording extended fine structure in EELS at higher energies is that such EXELFS spectra are generally cleaner. The first reason is that the probability is reduced that the tail of the EXELFS spectrum of one element overlaps with a core-loss edge from another element—because the absolute spacings between edges grow with increasing energy. The second reason is that the heavier elements typically have only L-, M-, and N-edges at energies below 2 keV, which have a more complicated inner structure than the K-edges and, therefore, are more complicated to fit using structural models.

We illustrated this with EXELFS measurements for the Cu K-edge at 9.0 keV and the Mo K-edge at 20.0 keV. We processed the EXELFS data using ATHENA software, which is routinely used for an XAS analysis in the synchrotron community. We benchmarked the Fourier-transformed extended fine structure of our EXELFS with similarly processed EXAFS data and found a very good agreement. Furthermore, we performed a quantitative fitting analysis, as typically applied to EXAFS data, and obtained element-specific bond lengths that closely match the literature values. In particular, metallic Cu, Cu₂O, and CuO can be clearly distinguished based on the fitted bond lengths, indicating that these phases can be identified in an unknown sample on a submicrometer scale by Cu K-edge EELS, especially when the corresponding reference materials are measured together with the sample under the same experimental conditions. This benchmark further proves that the rich databases and software packages available for XAS can also be exploited for assessing local coordination, structural parameters, and oxidation states of inhomogeneous materials based on measurements with the high lateral resolution now enabled by EELS. This adds a new information channel to the imaging, diffraction, and compositional analysis capabilities of the S/TEM.

Last but not least, we pushed our EELS setup to the limits by recording the Sb K-edge at 30.5 keV. At this extreme high-energy loss, the energy resolution is still close to that of XAS but the signal-to-noise in the EELS spectrum is too low for analysis of the fine structure. We attribute this reduced data quality to the drop in the cross-section (which scales approximately as $E^{-1.5}$) and the increase of the solid angle to which the signal is scattered (which scales approximately as E^2). It is noteworthy that the present study was undertaken with a scintillator detector; thus, the use of a direct electron detector with no or minimal noise may further improve performance in the future. In the end, the limits of lateral resolution and attainable energy loss of EXELFS will be determined by the beam sensitivity of the examined materials. Given the above, it is conceivable that an XEELS technique may be more suitable for hard materials that are not so beam sensitive and less applicable to softer materials that damage more easily under the electron beam.

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