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Electron energy-loss spectroscopy (EELS); comparison with X-ray analysis

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ABSTRACT

Analytical electron microscopy offers two main techniques of interest to materials science: electron energy-loss spectroscopy (EELS) and energy-dispersive x-ray analysis (EDX). The scientist is confronted with the choice of one of the two for the problem under consideration, although it is possible to employ both simultaneously. It is therefore important to know what to expect from each of the two techniques to assess which one is more likely to yield the desired information. Here both are compared to provide help in making that decision. The various aspects are illustrated with recent applications of both techniques in the research on interfaces in ceramics. Emphasis is put on the analysis of additional information contained in EELS, because this contributes to the understanding of bonding and chemistry inside the specimen.

1. INTRODUCTION

Many problems in materials science require that a small amount of an impurity is detected, for example the segregation to an internal interface. In the past EDX has often been the technique used for such microanalysis. Ease of use, immediate interpretable qualitative information about the presence of elements and straightforward quantification have made EDX a popular technique. Recently EDX has been extended to light elements (down to boron) with ultra thin window or windowless detectors [1]. Formerly the analysis of such elements could only be achieved with EELS. As far back as 1975 it was predicted that - for light elements - the sensitivity of EELS is larger than that of EDX [2]. This was with serial data recording which was then the only available method. The introduction of parallel recording devices [3] for EELS in electron microscopy has brought progress in the field of core-loss spectroscopy because the sensitivity was increased substantially [4] [5]. A drawback of EELS is that features in spectra are not always immediately visible, but require analysis. This can not yet be fully automated, but rather demands the interaction with the analyst. The recent progress in data analysis methods is discussed in this paper.

This review is mainly concerned with the analysis of grain boundaries and interfaces in ceramics. To address these questions high spatial resolution is required. Therefore we concentrate on experiments which can be performed in a dedicated scanning transmission electron microscope (STEM). Many of the points made are, however, also applicable to analysis in a conventional transmission electron microscope (TEM). Examples from our own experience were selected to illustrate the points we want to make about EELS and its comparison to EDX. The experiments were carried out using a VG HB501 STEM equipped with a high resolution pole piece, parallel EELS (Gatan 666 PEELS) and ultra-thin window high-purity germanium EDX analyzer (Tracor Northern 5500).

This paper is organized as follows: In the next section standard questions are addressed such as detection sensitivities and spatial resolution. The emphasis is difference spectroscopy at interfaces. This is important in the analysis of inhomogeneous specimens and progress has been made in EELS recently. Then special techniques in EELS are discussed, which do not have a counterpart in x-ray spectroscopy within the electron microscope. Before the conclusions are drawn an outlook is presented over the future of both techniques, especially about the prospects of elemental mapping with EELS.

2. ANALYSIS WITH EDX AND EELS

In this section the important aspects concerning analysis with EDX and EELS are summarized. The items which will be discussed in turn are listed in table 1. We concentrate on the points where the discussion is ongoing and progress is still being made.

2.1. EASE OF TECHNIQUE

In general EDX detectors are simple to use. The data can be interpreted easily in a qualitative way. A quick overview of the elements present in the sample is obtained. It is slightly more difficult to obtain data in EELS. The big drawback, however, is that the data can not always be interpreted immediately.

2.2. SPATIAL RESOLUTION

The spatial resolution of EELS and EDX have been compared in the past [6]. In EELS the entrance aperture of the spectrometer limits the volume of the specimen from which scattering events are detected. In EDX no such limiting aperture exists and electrons scattered through large angles which also generate x-rays contribute to the signal. This so called beam broadening makes the spatial resolution of EELS better than for EDX. As an example the calculated beam broadening [7] for 100 keV primary electron beam energy in 50 and 100 nm thick Al_2O_3 is 6.7 nm and 19 nm respectively. For EELS with a collection angle of 14 mrad these values are only 1.4 and 2.8 nm respectively and they are independent of other parameters. For EDX the beam broadening also depends on the specimen material. For thick specimens EDX is still possible, but at the expense of spatial resolution.

Although thickness does not decrease spatial resolution in EELS significantly, there is a problem with multiple scattering in thick specimens. Spectra can only be deconvoluted to a certain extent, and for larger thicknesses EELS becomes impossible. Also if the specimen has not been handled with care there might be contamination build-up during the experiment. EELS becomes impossible, as the changing thickness can not be accounted for. EDX on the other hand, is still applicable because the contamination (mostly carbon) does neither absorb x-rays strongly nor contributes significantly to the beam broadening.

A chemical profile of the oxygen-to-nitrogen concentration (figure 1) was measured across a planar defect in AlN, which is known to contain oxygen [8]. Apart from the surface oxide which is present on the specimen, there is more oxygen at the defect. The profile is about 1.5 nm wide as is expected for the STEM and the measured specimen thickness of 60 nm. Such a chemical profile measured across an atomically sharp interface in a thin specimen provides a measure of the spatial resolution in an analytical experiment. This direct method might be preferred to other methods, which determine the probe profile of the primary electron beam from the annular dark field intensity during a line scan across a sharp edge [9].

2.3. VISIBILITY

The visibility of a spectral feature is determined by the signal-to-background ratio. EDX has a small background arising from Bremsstrahlung and the visibility is large. Elements can be identified while the EDX spectra builds-up on the screen. This gives a quick and easy overview of which elements are present in the specimen. In EELS the signal is superimposed on a large background arising from inelastic

Table 1: Comparison between EELS and EDX.

	EELS	EDX
ease of use	medium	high
spatial resolution	good	beam broadening
contamination sensitive	yes	no
visibility (S/B)	low	high
peak overlap	no	can be severe
qualitative analysis	easy	easy
sensitivity (S/N) light elements	high	low
sensitivity (S/N) heavy elements	low	high
quantification	easy	easy
accurate quantification	complicated	complicated
energy resolution	high	low
extra information (ELNES, EXELFS, optical spectroscopy)	yes	no

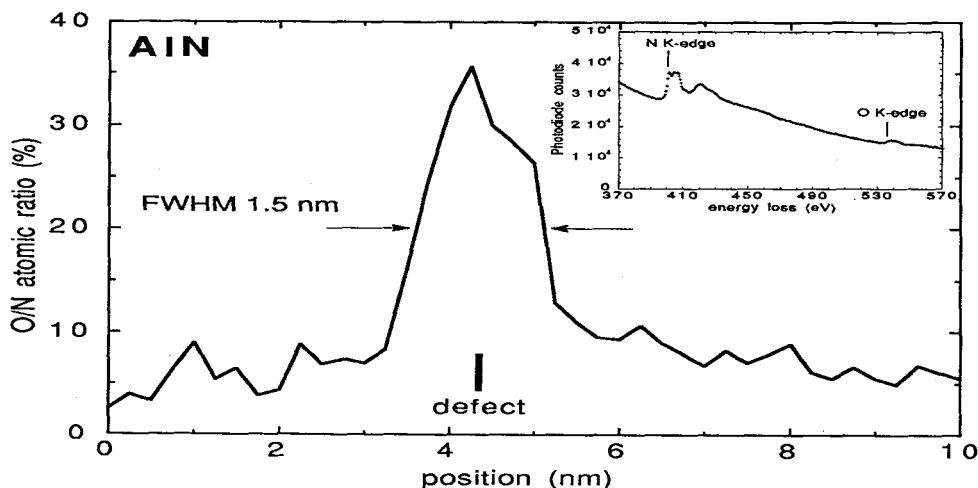


Figure 1: Chemical profile of O/N across a planar defect in AlN demonstrating EELS spatial resolution.

scattering from the valence electrons. The poor visibility in raw data prevents EELS from becoming a popular method. Automated data processing routines such as first and second energy-difference methods remove the background automatically and improve visibility [10]. There are, however, dangers in using such automated routines, as artifacts which would be detected by any skilled analyst may be screened.

2.4. PEAK OVERLAP

If several elements are present within the probed volume the signals may overlap. In EDX this may be a problem, especially if several light elements are present. Quantification can be complicated or even impossible. On the other hand EDX has the advantage of covering the whole energy range, i. e. all elements simultaneously. In EELS peak overlap occurs in few cases, because the energy resolution is much high. One spectrum, however, does normally not cover a sufficient energy range to detect all elements present. Therefore, the two methods are complimentary.

An EDX and an EEL spectrum measured from the same grain boundary phase of Si_3N_4 (figure 2) show this. In EELS (second difference mode to remove the background automatically) the three light elements Ca, N and O are clearly seen. The peaks are well separated and can be quantified. The Si L-edge is too low in energy and the Si K-edge too high to be seen in this spectrum. The EDX spectrum on the other hand reveals in addition to the three light elements Si and Yb. However, the EDX spectrum shows that while the visibility and the qualitative detection of these elements is straightforward, there will be severe problems due to peak overlap when quantification is tried. In this case EDX gives a quick overview of the sample composition. EELS can then be used for quantification of the detected elements.

2.5. DETECTOR ARTIFACTS

Some caution has to be exercised concerning detector artifacts. In EDX there are few, such as incomplete charge collection and escape peaks. They are well known and can be corrected for. For parallel EELS there are problems due to readout pattern and channel-to-channel gain variation of the detector [3]. These effects can be corrected for and on newer detectors they are reduced [11]. Afterglow of the detector after intense irradiation (e. g. zero loss) in EELS is a problem in low loss spectroscopy or if a spectrum is required for deconvolution together with a core-loss spectrum. All this adds some inconvenience to the use of EELS, but the problems can be overcome.

The channel-to-channel gain variation limits the detective quantum efficiency and hence the achievable signal-to-noise ratio. Data acquisition and processing techniques have been developed to overcome this problem [12]. Energy-difference methods are simple and they remove most of the effects. Two (three) spectra are acquired each shifted across the parallel detector. Their difference is effectively the derivative of the spectrum with respect to energy loss. The slowly varying background is removed and sharp edges are

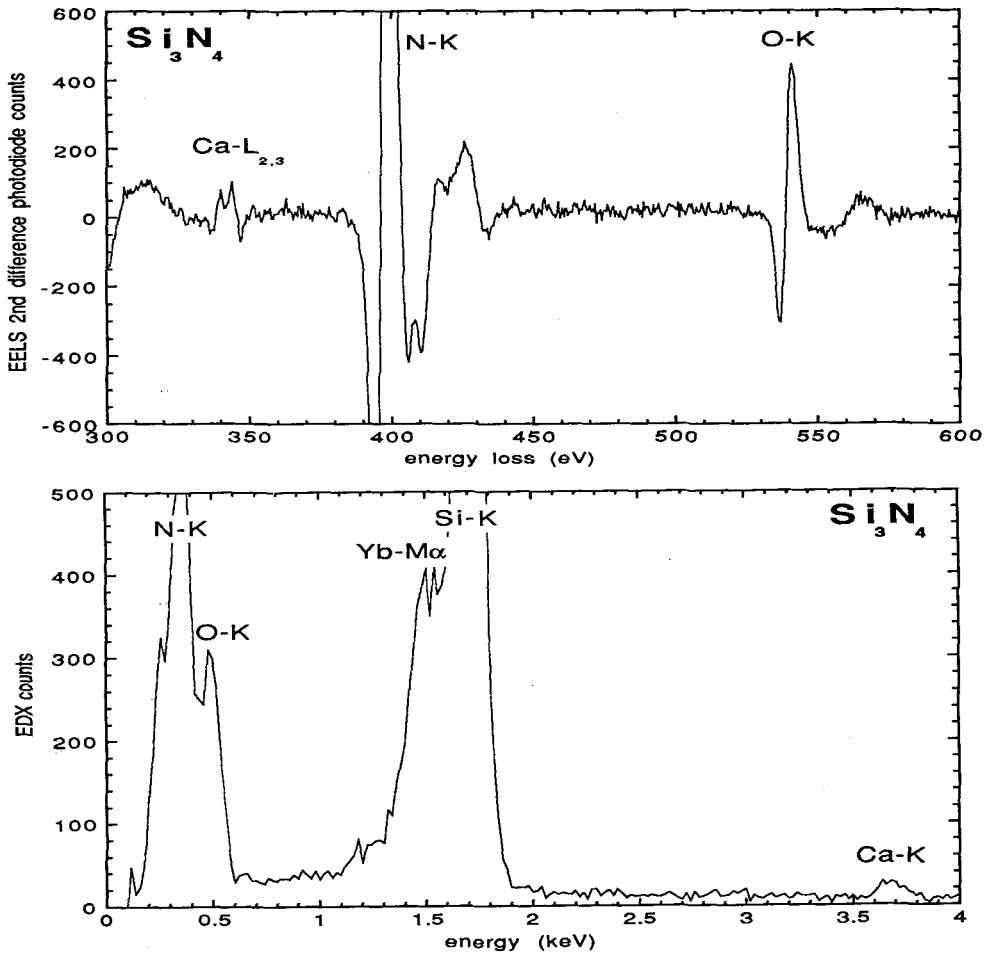


Figure 2: EDX and EELS from a grain boundary phase in Si_3N_4 illustrating the complementarity.

accentuated. Another possibility is the subtraction of a reference spectrum containing only the background. This method is called spatial-difference and will be discussed in section 2.8.

2.6. SENSITIVITY

The detection sensitivity is defined as the smallest amount of an element which can be detected in an analytical experiment and is determined by the signal-to-noise ratio (S/N) (*e. g.* [13]). The advantage of EDX is that all the signal is contained within a single narrow peak of a few channels at a certain energy, whereas in EELS the signal is spread over a large number of channels starting at the edge threshold. The total intensity in EELS is higher, because it is the primary event, but only part of it can be used. Whether EDX or EELS is more sensitive depends on the interplay of these factors [2].

For light elements it is well known that EELS has a higher detection sensitivity than EDX. Long ago [2] it was predicted that EELS is more sensitive than EDX for light elements. More recently this has been verified experimentally for elements up to $Z = 25$ [14]. EDX remains the technique of choice for heavier elements. Parallel recording devices have improved the detection sensitivity of EELS considerably. For example problems which could not be solved with serial data recording [15] have now been addressed successfully with parallel EELS [16] (section 2.8). Colliex [17] has reviewed the sensitivity of parallel EELS within a STEM. Typical values are 0.25 % of an impurity which corresponds to ten atoms. It has also been demonstrated that single atoms can be detected [18], but this is only possible in favorable cases.

2.7. QUANTIFICATION

The accuracy of quantification is steadily being improved for EDX by better theoretical determination of k-factors. This is especially a problem in the analysis of light elements. Similarly the accuracy of quantification in EELS has improved by more accurate calculation of inelastic scattering cross-sections. The ratio of two cross-sections, in analogy to EDX analysis called EELS k-factors, can not be calculated to an accuracy better than 10 - 20 % [19]. This is especially a problem for transition metals, where white lines occur at the L-edges. For both techniques k-factors can be determined experimentally to an accuracy of about 5 %. They depend, however, on the parameters of the experiment such as the primary beam energy, collection angle and detector. Therefore they are not easily transferable between different microscopes and detectors. To achieve high accuracy in quantification with either method, considerable effort has to be made to measure the k-factors for the particular system in use.

In material science, however, the spatial inhomogeneities of the specimen are often of interest, for example segregation to grain boundaries and other internal interfaces. Variations of the composition are just as important as absolute values. These are obtained easily in both, EELS and EDX, because approximate k-factor are sufficient. For EELS this has become prominent through the introduction of parallel EELS with user friendly software (Gatan EI/P).

2.8. SPATIAL-DIFFERENCE SPECTROSCOPY AT INTERFACES

One approach to reveal weak spectral features and remove the background is to subtract a reference spectrum which contains only the background. In this so called spatial-difference two spectra are recorded, one with the electron beam located on the region of interest (defect, grain boundary, dislocation, interface) and a second with the beam on the nearby matrix. The spatial-difference is derived by subtracting the (scaled) matrix spectrum from the spectrum of the region of interest. Quantification is readily achieved by integrating the residual intensity. This method assumes that the spectrum taken from the region of interest is dominated by the matrix component. No assumptions about the form of the background are necessary and any systematic background variations are automatically removed. Experimental conditions for spatial-difference are trivial (in a STEM) and data analysis is minimal.

The segregation of Y to interfaces in barium-titanate was investigated by spatial-difference EDX analysis. Two spectra were recorded, one from the grain boundary and one from the nearby bulk (figure 3). The two spectra are identical (indistinguishable in figure 3) except that the grain boundary spectrum shows the Y-K and Y-L lines which are not present in the spectrum from the bulk. The quantification gave 0.9 atom % of Y at the grain boundary. EDX was chosen because the sensitivity for a heavy element such as Y is higher than in EELS. EELS is not feasible in this case, because the Y L-edge is at 2080 eV energy loss and has therefore a weak signal. The Y M-edge at 157 eV is much stronger, but the detection of impurity elements with M-edges and their quantification is still relatively new [20].

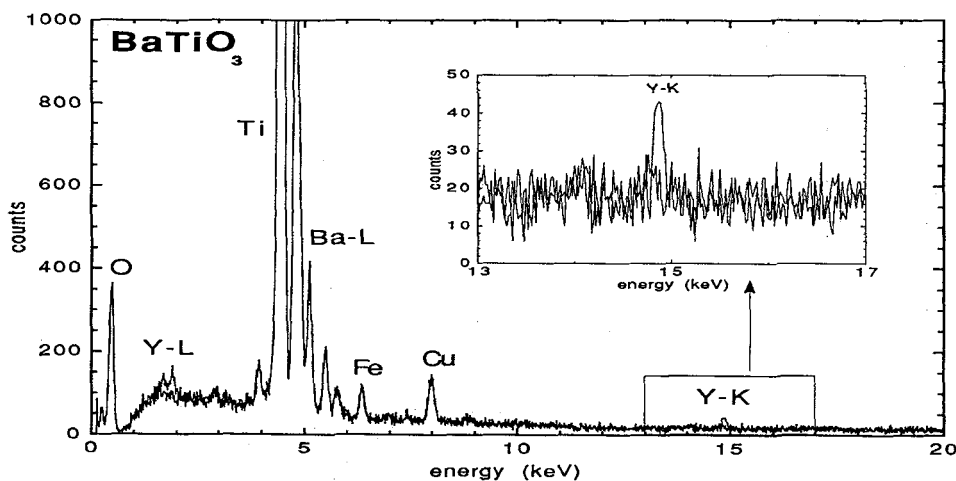


Figure 3: EDX spectra from a grain boundary and bulk BaTiO₃ revealing Y segregation.

Table 2: Evaluation of different methods to remove the background from EEL spectra.

	standard E-r fit	spatial- difference	energy- difference
removal of detector artefacts	difficult	automatic	automatic
structure in background removed	no	fully	only partly
visibility	after analysis	after analysis	immediate
quantification and data analysis	easy	easy	complicated
reference spectrum required	no	yes	no
near edge structure analysis	yes	yes	difficult
a priori information required	no	no	desirable

In EELS the spatial-difference has the advantage that the large background is removed automatically together with the detector artifacts (read out pattern and channel-to-channel gain variation) (table 2). While all difference methods achieve the same, spatial-difference can lead to a more accurate background extrapolation and thereby improve the detection sensitivity. This is especially true in the presence of systematic background variations, such as the extended energy-loss fine structure (EXELFS) of preceding edges.

An application of this is the detection of nitrogen at platelet defects in diamond [16]. The spatial-difference method was used with particular success, as it removes the underlying EXELFS signal originating from the preceding C K-edge (figure 4). The quantification gave about 1 % of nitrogen (75 atoms) in the sampled volume, which corresponds to 1/10 of a monolayer of N at the planar defect. This shows that N is a impurity rather than a major component of the defect. The extrapolation of the actual S/N down to 5 suggests that 10 times less N could have been detected, i. e. 0.1 % (8 atoms) or 1/100 of a monolayer.

The spatial-difference has a higher detection sensitivity than energy-difference or standard background extrapolation methods. This result was obtained when calcium segregation at grain boundaries in Al₂O₃ materials was studied. This is critical in attempts to understand physical properties of Al₂O₃. Spectra containing the Ca L_{2,3}-edge were recorded from a grain boundary in sintered Al₂O₃ (sample VC3 of [21]). The probed volume contained 1 % of calcium as determined by EDX analysis. The calcium was detected with energy- and spatial-difference in EELS. An evaluation of the S/N ratio for the three background removal methods showed that spatial-difference performed best (table 3). An extrapolation to a S/N of 10 gave a detection sensitivity for spatial-difference of about 0.04 atom %, which corresponds to 26 Ca atoms in the sampled volume (800 nm³) or 0.01 of a monolayer. These values are consistent with the detection sensitivity estimated for our experimental conditions [13].

We believe that in materials science, where the interest is in specimen inhomogeneities, the spatial-difference is preferable to energy-difference. Whilst immediate visibility of features in energy-difference

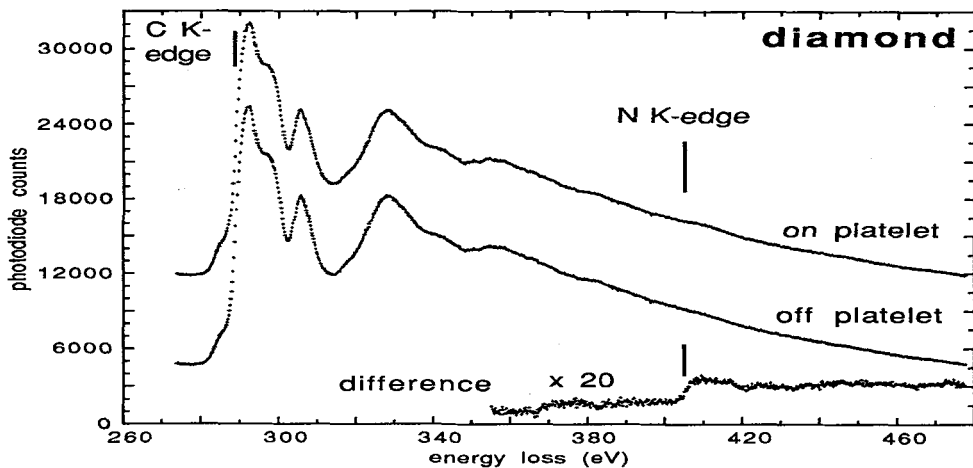


Figure 4: Spatial-difference EELS from a platelet defect in diamond revealing the nitrogen K-edge clearly.

Table 3: Experimental S/N for standard E⁻ fit, second difference and spatial-difference measured for calcium L_{2,3}-edge at a grain boundary in Al₂O₃.

method	signal (counts)	noise (counts)	S/N
standard E ⁻ fit	31278	369	85
second difference	16450	82	201
spatial-difference	16730	68	246

may be superior, spatial-difference has a better detection sensitivity. Another clear advantage of the spatial-difference involves the study of near-edge structure of the impurity element, yielding information on the atomic structure and chemical bonding of internal interfaces (section 3.1).

3. ADDITIONAL BENEFITS OF EELS: SPECTROSCOPIC INFORMATION

In this section features of EELS are discussed which have no counterpart in EDX emission. The energy resolution with cold field emission as in the VG STEM is typically about 0.5 eV in EELS. With this energy resolution it is possible to examine the fine structure of the absorption edges (energy-loss near-edge structure (ELNES) and extended energy-loss fine structure (EXELFS)) and further to do valence-loss spectroscopy. These techniques are analogous to the more familiar techniques with x-rays (synchrotron radiation) and optical experiments (XANES, EXAFS, e. g. VUV spectroscopy). The same information is hence obtainable from EELS, but with the added benefit of high spatial resolution, yielding information on a local scale.

The study of inhomogeneities in the specimen such as defects, grain boundaries and interfaces with these techniques is relatively new, as only parallel EELS has made it feasible. Progress in the theory and data analysis of these methods make them more interpretable. The information that can be obtained is partly complementary and partly additional to the information obtained from structural atomistic modelling and high resolution electron microscopy (HREM). Both of these are quite well advanced in the case of pure specimens, but are poor if impurities are present. In real materials, however, the interest is often focussed on the effect of impurities, which can be studied by analytical electron microscopy. Especially ELNES is successful in obtaining information from grain boundaries and defects to reveal details about the atomic structure.

3.1. ELNES

The information present in ELNES is often complicated, and the interpretation has thus far been mostly qualitative [22]. Often using the concept of "chemical fingerprints" for the determination the atomic coordination it is possible to get information about the local atomistic structure. Similar ELNES suggests a similar atomic environment. Calculations of ELNES, which follows the same theory as XANES, have so far been carried out for bulk materials. In the electron microscope ELNES can now be measured spatially resolved from interfaces and interpreted qualitatively. The calculation of ELNES given the atomistic structure of an interface is an approach which will be used in the future to support experiments (ELNES, HREM) and theory (atomistic structure modelling).

In spatial-difference from platelet defects in diamond (section 2.8) the ELNES of the nitrogen K-edge can be seen. In figure 5 the near-edge structure of carbon and nitrogen are superimposed with the energy scale measured from the edge onset. There is a striking similarity between the two, indicating that the local atomic environment is similar for both elements. This suggests that nitrogen might be substitutional in the carbon lattice.

A more complex problem is the structure of the near $\Sigma 11$ grain boundary in an ultra pure sapphire bicrystal. No impurities were detected either with EELS or by EDX. This boundary was examined by spatial-difference ELNES [23]. The subtraction of the matrix spectrum as a reference from the grain boundary spectrum yields the grain boundary component of the ELNES (figure 6). The detailed interpretation of this information showed that the coordination of the aluminium atoms at the grain boundary is reduced and that the interatomic distance between these aluminium atoms and the next nearest oxygen atoms is increased by 2 % with a spread in the distribution of bond lengths. This method of extracting and interpreting the ELNES arising from the atoms at the interface is new. It offers exciting prospects in the understanding of interfaces and grain boundaries.

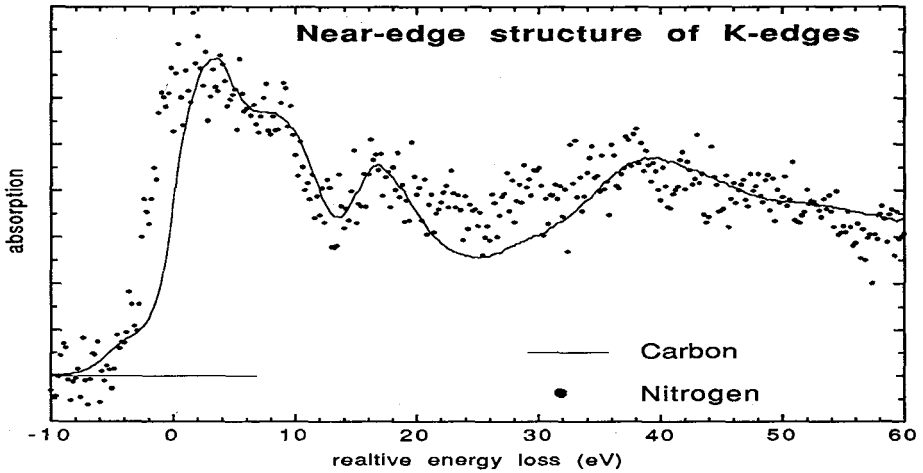


Figure 5: The ELNES of C and N K-edges in diamond is similar suggesting similar atomic environment.

3.2. EXELFS

EXELFS gives information about the radial distribution function of the investigated material within the specimen [13]. Data analysis is relatively straightforward. In the past, however, the detected EXELFS signal has been too weak to be employed usefully in the investigation of atomistic structure. With the advent of parallel EELS it will be possible to investigate interatomic spacings in the vicinity of interfaces.

3.3. OPTICAL SPECTROSCOPY

The valence part of the energy-loss spectrum has been used for a while to derive the dielectric function from materials on a local scale. Interest has been given to special geometries, such as interfaces, which were used to verify the classical dielectric theory [24] [25] [26]. Recent developments in vacuum ultraviolet optical spectroscopy have enabled quantitative critical point analysis of dielectric data enabling direct comparison to the band structure [27]. Such analysis can also be applied to data obtained by EELS. A comparison of data from both techniques for Al_2O_3 has shown a close correspondence (Roger French, DuPont, private communication). Therefore it is possible to analyze EELS data quantitatively. By taking valence-loss spectra from interfaces or grain boundaries and compare them with the spectra obtained in the bulk material the change in the electronic structure can be determined. Preliminary results are two valence

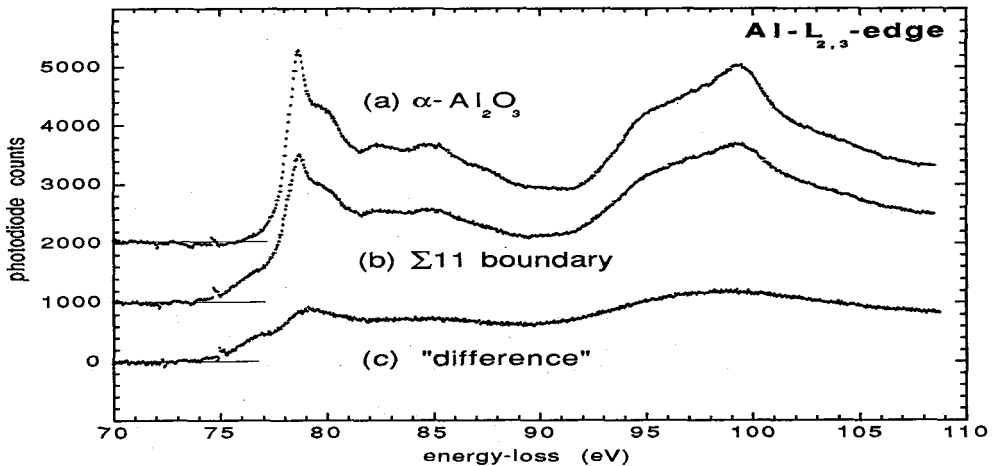


Figure 6: $\text{Al L}_{2,3}$ -edge ELNES of the $\Sigma 11$ grain boundary in a sapphire bicrystal. The spatial-difference ELNES reveals information about the bonding and coordination of the aluminium atoms at the boundary.

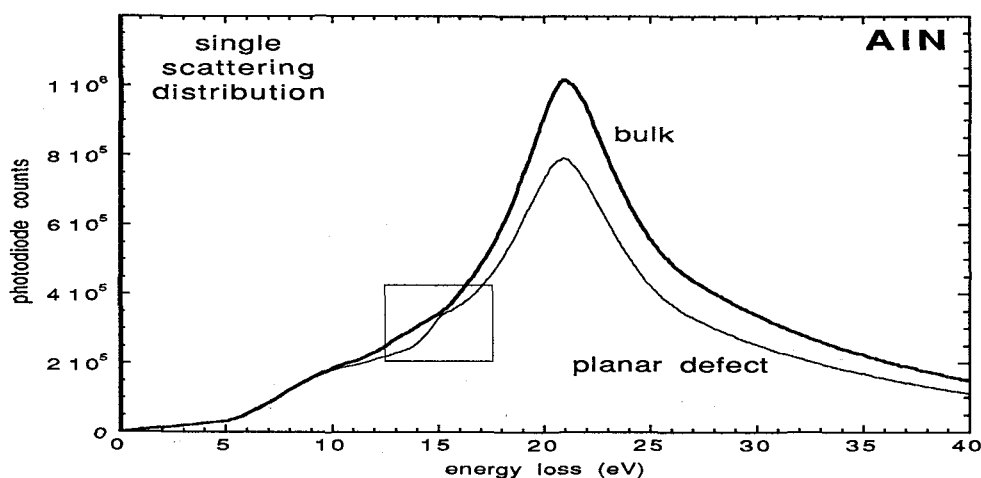


Figure 7: Valence-loss EELS from bulk AlN and a planar defect.

energy-loss spectra recorded from AlN (figure 7), one from the planar defect which contains oxygen (section 2.2) and one from bulk AlN nearby. There is a marked difference between these two spectra.

4. FUTURE: ELEMENTAL MAPPING WITH EELS

To understand the microstructure of a material it is often helpful to have an elemental map. EDX signals within the electron microscope are in general too low to yield a useful digital map in a reasonable time span. The intensities in EELS on the other hand are sufficiently high to produce such elemental maps. There are two approaches. On one side energy filters in conventional TEMs (Zeiss 902 with omega filter, Gatan energy filter for TEM) allow the collection of energy filtered images. If images are acquired for three energy losses, two before and one after an edge in the spectrum, the background can be subtracted and the residual intensity can be used to construct an elemental map. The other approach is to collect an EELS for each image pixel in a STEM [28] [29] [11]. There may even be prospects of atomic resolution spectroscopy in conjunction with Z-contrast imaging in the STEM [30]. The time needed to collect a sizable signal depends on the field of view. For low magnifications a TEM with energy filter provides more intensity per pixel, whereas at high magnifications the STEM is better. A comparison of the available beam currents for the VG STEM and the ZEISS omega filter TEM suggest that the two microscopes should give comparable results for an energy filtered image at a magnification of 1 M. For an elemental map which contains three elements such as C, N, and O nine images have to be acquired in the TEM whereas a single STEM spectrum image contains all the useful information. Thus the two microscopes would be equivalent at about 300 K magnification. In the study of interfaces high magnifications are necessary and therefore a STEM will be superior not only because of the higher signal intensity but also because of better spatial and energy resolution. It can even be envisaged that in particularly favorable cases not only the elements are mapped, but also their ELNES.

5. CONCLUSIONS

The inherent wealth of information contained in EELS makes this technique less suitable for routine, computerized analysis. Data processing in EELS has to be interactive and the skill and the knowledge of the analyst are required to make full use of the available information. This is on the other hand the strength of EELS, as a knowledgeable analyst will be able to extract information from EELS which can not be obtained otherwise. This does not make EDX obsolete. The two techniques should rather be viewed as complimentary, each contributing vital information to the solution of a particular problem. There should be, however, a good sense of what are reasonable aims with each of the two methods, so a problem can be solved as quickly and comprehensively as possible, rather than wasting time on the wrong approach.

EDX does not offer any extra information. Progress has been made to the instrumentation for the detection of light elements. Otherwise the development is concentrated on improving the quantification to higher

accuracy. EELS on the other hand is a field in which still many innovations are made and methods which have been discussed theoretically for some years are now being accomplished. Only with the recent and future developments in instrumentation, which allow full use of the available information, and a better theoretical understanding the full potential of EELS will be reached. In the next few years this development will gain further momentum through the exciting applications in materials science.

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