AN ELECTRON ENERGY LOSS SPECTRAL LIBRARY AND ITS APPLICATION TO MATERIALS SCIENCE

N. Zaluzec

To cite this version:
N. Zaluzec. AN ELECTRON ENERGY LOSS SPECTRAL LIBRARY AND ITS APPLICATION TO MATERIALS SCIENCE. Journal de Physique Colloques, 1984, 45 (C2), pp.C2-429-C2-432. <10.1051/jphyscol:1984297>. <jpa-00224012>
AN ELECTRON ENERGY LOSS SPECTRAL LIBRARY AND ITS APPLICATION TO MATERIALS SCIENCE

N.J. Zaluzec

Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

Résumé - On présente un catalogue de données spectrales en pertes d'énergie des électrons pour des niveaux profonds. Des applications à des problèmes typiques en science des matériaux sont montrées.

Abstract - The format as well as the motivation behind the development of an EELS library of inner-shell edge profiles is outlined and its application to typical problems in materials research discussed.

I - INTRODUCTION

The use of electron energy loss spectroscopy (EELS) in conjunction with a transmission electron microscope (TEM) is becoming an important technique for materials characterization. Unlike its x-ray energy dispersive spectroscopy counterpart (XEDS), the measured intensity profiles can be extremely complex and thus tables of edge energies are not always sufficient to uniquely identify all elemental species. As such it becomes relevant to know the systematic changes in the profiles for core-loss edges across the periodic table as well as in various phases or compounds. It has now been two years since the first experimental library of this sort has been distributed /1,2/ and it has proven invaluable to the routine use of EELS in material science. In complex multi-element systems a simple atlas of edge shapes /3/ is frequently insufficient, since inevitably, spectral overlap occurs obscuring or complicating the desired information. In these situations, the use of library spectra for the purpose of identification and removal of spectral overlaps can provide the analyst with semi-quantitative results in situations which would have been previously considered insoluble.

II - FORMAT OF THE LIBRARY

Distribution of this library is currently in two forms. The first as intensity profiles and the second as ASCII data files on appropriate mass storage devices (usually floppy disk) for use with compatible computer systems, both of which are briefly outlined below.

Arranged as a function of atomic number, a typical entry from hardcopy format of the second edition of this library contains the following information. At the top of each page is a short description of the specimen, method of preparation, and experimental conditions employed during the measurement (i.e. accelerating voltage, resolution, beam convergence, scattering angle, relative specimen thickness, etc.), followed by four spectra. The first spectrum is the low loss profile, while the second is the high loss region surrounding the characteristic edge; both these are unprocessed experimental data. The third spectrum presents the edge profile after background subtraction. Here either a conventional A/E^T, polynomial, or log-polynomial background model (which ever is most appropriate) is used to remove the continuous background under the edge, while the last profile shows the edge after removal of multiple scattering by deconvolution.

*Work supported by the U.S. Department of Energy
This final spectrum should, therefore, represent the single scattering profile with thickness effects mathematically removed. When sufficient data exists about the specimen (i.e. its actual composition and thickness) the profiles are converted into absolute cross-section measurements, otherwise the data is simply presented as counts/channel. Each edge, when feasible, is measured under at least two scattering angles. The first a value corresponding to an angle $0 \geq \frac{E_0}{2E_C}$ which yields an optimal peak/background ratio, and is usually within the dipole approximation. Here $E_0$ is the relativistic electron energy $[\frac{1}{2}(mc^2)^2]$ and $E_C$ the critical excitation energy of the respective shell. The second is at a very large scattering angle $\sim 50-100$ mr to allow non-dipole transitions to be visible. In addition, all intensity profiles are distributed in an unbound (loose-leaf) format so that the users may simply update their copies by the addition of individual pages rather than having multiple bound copies of uncorrelated data. This was deemed the most appropriate format since such a library can in reality never be complete and other experimentalists may wish to contribute to the scope of this work as a benefit to the general scientific community. The Electron Microscopy Center of the Materials Science and Technology Division at Argonne National Laboratory has established an EELS reference data base for this purpose and all those interested in contributing to this library are welcome. Copies of the complete EELS library are available without charge by submission of a written request. Figure 1 is a brief selection of edge profiles (after background subtraction) for the most frequently observed edges in materials analysis from Lithium ($Z=3$) through Silver ($Z=47$).

At present a limited distribution of the library is also being explored using magnetic mass storage. The major limiting factor here, is the wide variety of data formats present on the computer data storage diskettes being used by the XEDS/EELS Multichannel Analyzer manufacturers. These copies are being distributed together with a generic translation program which allows the data files to be converted into the different formats used on the individual microcomputers. When the details of this mode of distribution have been finalized all those on the mailing list will be notified. In this mode, however, it will be necessary for the individual user to supply their own mass storage media, copies will still be provided gratis.

III - APPLICATION TO MATERIALS

Aside from the use of an EELS library as a simple atlas of spectral shapes, the most important aspect of this study is the ability to provide a direct measurement of partial ionization cross-sections for the various elements studied. This is particularly important for quantitative measurements since the hydrogenic models developed by Egerton /4,5/ allows only a finite range of elements to be analyzed. Potentially the data base of cross-section values being developed can be used in the refinement of parametric equations used for quantification. This is particularly true for the case of higher $Z$ materials where virtually no simple formulations exist for L, M, or N shell transitions /6/.

A second and equally important application of this library involves the direct application of reference spectra for data reduction purposes, which presupposes access of data files through an appropriate computer based data analysis system. The present system in use at ANL consists of a DEC LST 11/2 using the Version 4.0 RT-11 operating system, a Tektronics 4010 graphics terminal and RX02 floppy disk mass storage. In addition, an EDAX SW9100/70 or an ORTEC EEDSII multichannel analyzers both having DEC hardware are utilized as appropriate.

The study of light element distributions in precipitates of steel is a good example of the problems encountered during a "real" application of EELS to materials research. Shown in figure 2 are partial spectra from precipitates formed upon thermal aging of type 316 Stainless Steel /7/. These spectra were obtained from precipitates identified as MC, $M_23C_6$, and Laves phases. XEDS analysis of each routinely yields the relative composition of all species with $Z > 11$, however the low $Z$ compositions were still unknown. EELS in the case of
the MC and the M23C6 phases clearly identifies the presence of a Carbide, since it is easy to show, that the Carbon measured here is not amorphous by the presence of the near-edge fine structure clearly visible at the Carbon K shell onset (~283 eV). Amorphous carbon is nearly featureless /2,3/ with the exception of a weak transition at the edge onset. The difficulty in these analyses arises due to the presence of high atomic number alloying elements, in this case Molybdenum. Unfortunately for the analyst, Mo has an M-shell edge in the energy loss region between 200 and 800 eV loss. As an added complication, the shape of this edge is very extended having the classical delayed maximum /2,6/ and a few relatively sharp but small M32 transitions in the vicinity of 400 eV loss. A partial EELS spectrum from nominally pure Mo is shown at the bottom of figure 2. Although one can easily identify the first two spectra as Ti-based and Cr-based Carbides, quantification requires measurement of the net integrals of each element's edge profile over a substantial energy window (~100 eV). Clearly, for both these cases the severe overlap between the Mo M-shell and the C K-shell would preclude analysis. By recalling, from a library file, the edge profile from pure Mo, subtracting its background then scaling the resultant to the M shell onset just visible before the C K-shell and finally subtracting this scaled Mo M-shell profile from the carbide spectra allows the analyst to obtain the net carbon integral. It then becomes possible to proceed with the analysis at least on a semi-quantitative basis. This procedure presumers that the effects of chemical shifts between the different bonding states of Mo are negligible, that both spectra are obtained from sufficiently thin regions that multiple scattering effects are minimal, and that the nominal experimental conditions are similar. The details of these assumptions are currently under investigation; however, even in light of these approximations it still allows the analyst to proceed with at least a semi-quantitative analysis. An even more complex situation exists for the Mo-rich Laves phase. One would certainly be remiss in attempting to quantify the carbon content of this phase at this time due to the necessity of subtracting two large quantities and analyzing the small residual. It is pertinent, however, to point out that in this situation, the well resolved edges near 400 eV cannot be simply attributed to the M32 transitions of Molybdenum, and one concludes that an additional element, in this case Nitrogen, is present. Such a result would have been impossible using a XEDS system, even of the Windowless variety, due to their relatively poor resolution in this energy regime.

IV - CONCLUDING REMARKS

An electron energy loss spectral library can be an invaluable tool in materials research from a fundamental as well as a practical standpoint. Although it will not alleviate all the complications associated with quantification, this type of library can help to elucidate details of spectral profiles previously found intractable. This work was supported by the U. S. Department of Energy. The author also wishes to express his gratitude to the organizing committee for partial financial support provided to attend this meeting.

V - REFERENCES

Figure 1. A selection of EELS edge profiles after background subtraction for the elements Li through F (K shell); Sc through Ge (L shell); and Y through Ag (M shell). Energy scales of 5, 10, and 20 eV/division as indicated. Spectra are arbitrarily displaced for display purposes.

Figure 2. Partial EELS spectra after background subtraction for a Ti-based (MC) carbide, Cr-based (M23C6) precipitate and a Mo-rich Laves phase in thermally aged type 316 Stainless Steel. For comparison, a partial spectrum from pure Molybdenum showing the M-shell transition which occurs over the same energy regime is also shown. Note that the presence of the Mo M-shell in the MC, M23C6, and Laves phases precludes quantification without first removing the Mo spectral overlap.