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An Electron-Energy-Loss-Spectra Library*

N. J. Zaluzec
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

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AN ELECTRON-ENERGY-LOSS-SPECTRA LIBRARY

N. J. Zaluzec

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

The use of electron energy loss spectroscopy (EELS) in conjunction with a transmission electron microscope (TEM) is becoming an increasingly important tool for state-of-the-art materials research and as a result it becomes correspondingly important to have accurate information about the shape and positions of the inner-shell and plasmon losses which may be observed. Although the general characteristics of an energy loss spectrum are reasonably well-known, tables of atomic energy levels are not always sufficient to uniquely identify all features in a given spectrum. The systematic variation on an element-to-element basis across the periodic table can be substantial and has not yet been documented in a single reference source. In conjunction with the basic research program of the Materials Science Division of ANL, a wide range of specimens has been studied using EELS over the last few years; resulting in a fairly extensive data base being accumulated. This work is now being prepared for general distribution to the scientific community in the form of a spectral library and will be periodically updated as additional measurements are obtained. At present this study contains in excess of 100 edges and their corresponding low loss spectra for the elements: Li, Be, B, C, N, O, F, Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Y, Zr, Nb, Mo, Pd, Ag, Cd, In, Sn, Hf, Ta, W, Pt, Au, Pb and Bi, recorded from nominally pure elements or stoichiometric compounds.

Measurements were made on a Philips EM400 TEM fitted with a $\pi/2$ magnetic sector energy analyzer, using an incident beam energy of 120 keV over the energy loss range 0-5 keV; at energy resolutions varying from 2-10 eV as appropriate. For each element both the low loss (0-100 eV) as well as each

observed core-loss edge (K, L, M, N...), are recorded together with relevant experimental information (acceptance angle, specimen thickness, crystalline orientation etc.). In the case of compounds or alloys containing similar edges, but in different chemical and/or structural states, multiple spectra are provided for cross-referencing and relative comparisons. For example, the nickel edge in pure Ni and NiO; the oxygen K edge in MnO, Al_2O_3, Y_2O_3, NiO; or carbon K edge in amorphous carbon, graphite, and diamond can be readily observed and compared with experimental measurements as an aid in analysis and interpretation.

Initial distribution of this library will be in the form of intensity profiles as illustrated in figure 1; however, this information will eventually be made available as ASCII data files on suitable mass storage medium (DEC RX01 floppy disks) for use on compatible data acquisition systems. At present, corrections for multiple scattering effects have not been applied to the data, but, it is planned to incorporate this as part of the general distribution. Each edge will then be presented in at least two forms; namely, the raw data and a corresponding deconvoluted single scattering profile.

One of the principle motivations to the documentation of core-loss profiles is that virtually every element studied using EELS will show departures from the theoritical profile as calculated using current hydrogenic[1] or quantum mechanical[2] cross-section models. In general, these calculations are based on atomic models and cannot predict band structure or bonding effects which will be present in actual solids. An example of this discrepancy can be seen by comparison of figures 2 and 3. Figure 2 is taken from the work of Rez and Leapman[2] showing the computed L and M shell EELS profiles for selected elements, while figure 3 illustrates corresponding experimental data taken from this work. Although the experimental conditions

used during these measurements were not identical to those employed for the calculations, the differences between these spectra are principly due to solid state effects. In addition to acting as an atlas of spectral shapes, the study of inner-shell core losses allows a direct measurement of the relative partial ionization cross-section for each edge and element investigated. This information can become invaluable in assessing the various theoretical models used in EELS quantification and potentially can be used in the development of parametric equations to simplify the lengthy and complicated quantum mechanical cross-section calculations. Finally, microanalysis of light elements in medium or heavy atomic number matrices is sometimes precluded, due to the number and complexity of the inner-shell edges from higher Z elements overlaping the K shells of lighter elements. For example, the molybdenum M shell extends from roughly 225 to 550 eV and can result in severe overlap of the carbon and nitrogen K shells at ~ 284 and ~ 400 eV respectively.[3,4] Microanalysis in situations such as this can still proceed by recalling a reference spectrum of the appropriate edge (i.e. Mo M-shell), superimposing, scaling, and finally subtracting this modified spectrum from the experimental data and then proceeding with analysis of the remaining edges.

Since it is not practical to document the entire EELS library in these proceedings, the remainder of this text will summarize the general features of the spectra within the library. Copies of the present library are available upon request.

Lithium (Z=3) to Fluorine (Z=9)

For these elements one is studying K-shell (1s) transitions, however, only for metallic beryllium and amorphous carbon does one observe edge profiles which approximate a hydrogenic shape. The elements Li, B, N, O and F where all studied as compounds and when measured at moderate energy

resolution ($\leq$ 3 eV) exhibit distinct near-edge fine structure which varied from one compound to another; for example, the oxygen K shell in NiO, Al_2O_3, Y_2O_3, $CaTiO_3$, MnO and SiO_2 is markedly different in each case. In general, insulators exhibit strong near-edge fine structure, corresponding to the existance of unoccupied bound states just above the Fermi level.

Magnesium (Z=12) to Silicon (Z=14)

Both K shell (1s) and L-shell (2s,2p) transitions are available for microanalysis in these elements. In pure element form, the K-shells exhibit hydrogenic-like shapes, however upon formation of compounds the near-edge fine structure can become quite pronounced as discussed above. The L shell transitions all show a delayed maximum as predicted by Rez and Leapman,[2] however, sharp transitions at the L_{32} onset can be resolved particularly in Si.

Calcium (Z=20) to Selenium (Z=34)

The K-shell transitions of these elements are no longer realistically studied as their energy losses are greater than 4 keV. The most useful edges for EELS work become L-shell (2s, 2p) transitions. For the elements Ca through Ni the onset of the L_3 and L_2 edges is especially prominent corresponding to the excitation of $2p^{3/2}$ and $2p^{1/2}$ electrons into empty d-band states. The L_1 edge (2s) is very weak and is seldom detected. At Cu the d-band fills, and the sharp transitions marking the L_3 and L_2 edges disappear. By the time Ge is reached a classical delayed maximum is observed as in the case of Mg and Al; although the L_1 shell is now increasing in intensity and visiblity. It should also be noted that all these elements have significant M shell (3s, 3p, 3d) transitions and care should be taken not to misinterpret these edges as the presence of additional elements.

Yttrium (Z=39) to Tin (Z=50)

The L shells of these elements follow almost identically their fourth period counterparts. Sharp L_3 and L_2 transitions are observed from Y to Pd disappearing at Ag (corresponding to a full 4d-band), however, as a practical point their energies (2-5 keV) are usually beyond the range used for conventional EELS studies (0-2 keV). The M shells form the most prominent features of the EELS spectrum covering the 100-1000 eV range and are characterized by a large delayed maximum at the M_5 M_4 ($3d^{5/2}$, $3d^{3/2}$) onset. In contrast, the M_3 and M_2 edges are relatively sharp corresponding to $3p^{3/2}$, $3p^{1/2}$ excitations to the unfilled 4d band; however at Ag these edges, as in the case of the sharp the L_3 L_2 transitions, disappear. The M_1 (3s) edge was never observed under the experimental conditions used. N-shell (4s, 4p, ...) transitions begin to appear at very low energy losses (<100 eV).

Hafnium (Z=72) to Bismuth (Z=83)

For all practical purposes the only shell available for microanalysis here is the M. As in the fifth period elements a large delayed maximum is observed, superimposed upon which are reasonably sharp M_3 M_2 edges. The N shell transitions are just barely discerable above background and in most cases will not be detected due to their extremely low cross-sections. O shell transitions are becoming reasonably strong and dominate the low loss spectrum (< 100 eV).

Rare-Earths and Actinides

No measurements have been made for these elements during the initial phase of this study, however, Krivanek and Ahn[5] have observed sharp well-defined transitions at the M_5 M_4 edges for several rare earth oxides and similiarly at the uranium O_{45} edge by Colliex et al.[6]. This correlates well

with the fact that the 4f and 5f bands are empty for these elements producing conditions similar to the 2p excitations in the transition metals.

Acknowledgements

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Figure Captions

Figure 1. Example of typical intensity profile and relevant experimental information from the EELS Library. At the top is a short description of element, specimen, and experimental conditions employed, below that the measured intensity profile having been corrected only for background. No corrections for multiple scattering have been applied to the data, however, relative thickness comparisons can be made by reference to the documented I_o/I_t values reported for each edge. Here I_o represents the net integral over the FWTM of the zero loss peak while I_t the net integral over the first 50 eV of the total spectrum. As the specimen thickness decreases the value of I_o/I_t approaches unity, and can be shown to be related to the ratio of specimen thickness to mean-free-path. Across the top of each spectrum are the corresponding limits for the X & Y axis of the figure. Thus, XMIN:XMAX: DIV correspond to the values of the minimum and maximum along the x-axis while DIV is the incremental value of the smallest indicated division on that axis.

Figure 2. Calculated L-shell (a) and M-shell (b) EELS profiles for an incident beam energy of 80 keV and acceptance angle of 10 mr. (Rez and Leapman ref. 2).

Figure 3. Experimental L-shell (a) and M-shell (b) EELS profiles for an incident beam energy of 120 keV and acceptance angle of 5.7 mr.

Element	Shell	Atomic Number
Carbon	K	6

Specimen

Type IA Diamond prepared by Argon ion-milling (specimen courtesy of P. Humble -CSIRO)

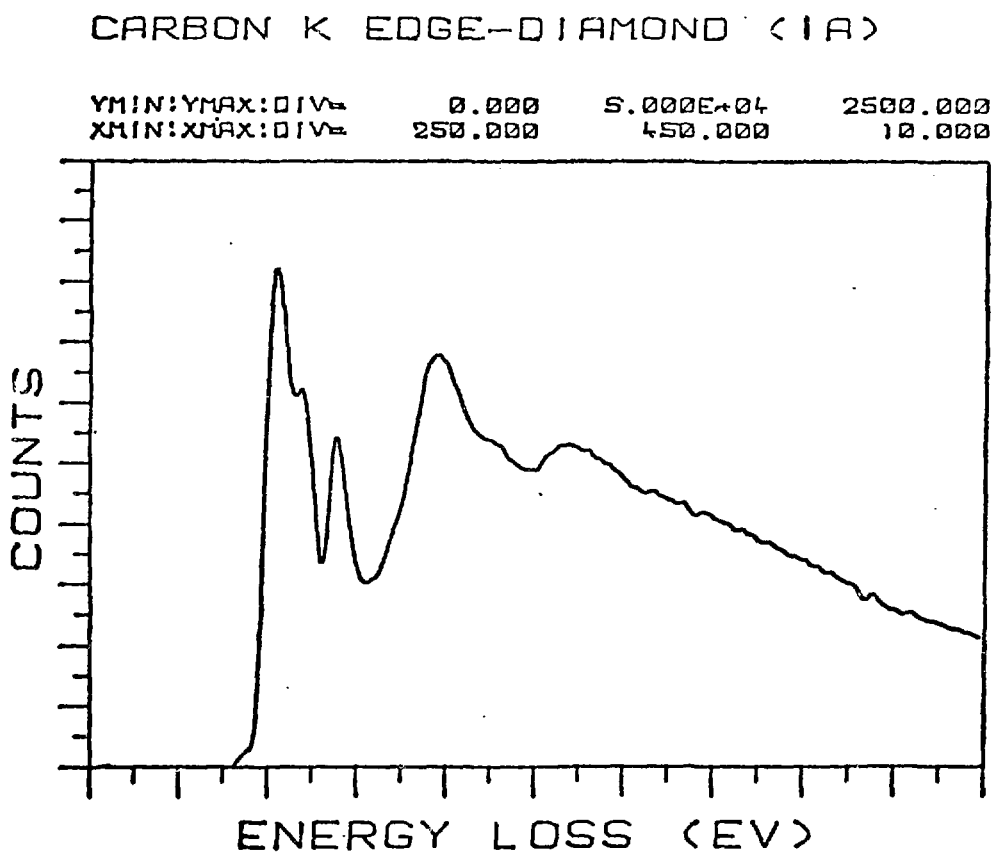
Experimental:

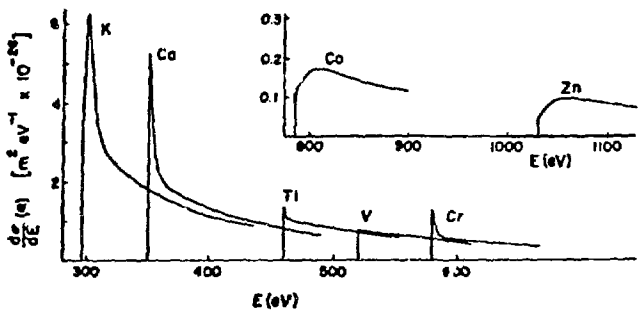
Incident beam energy	= 120 keV	Scattering Angle	= 2.6 mr
FWHM of Zero Loss	~ 3 eV	Incident beam divergence	~ 1 mr
Energy Calibration	= V L edge 3	I (FWTM)/I (50 eV) 0 T	= 0.543
Low Loss Peaks (eV)	24.4,32.8		

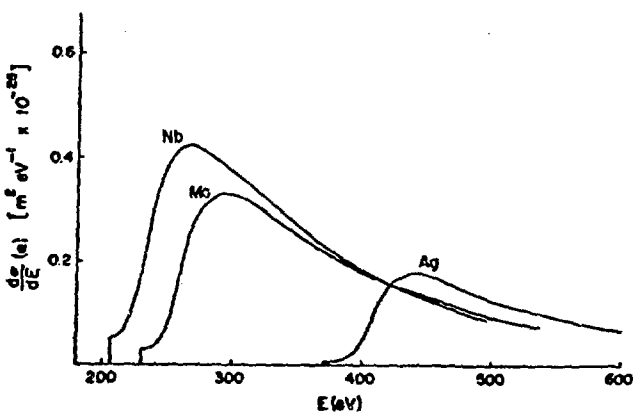
Pure Element Data

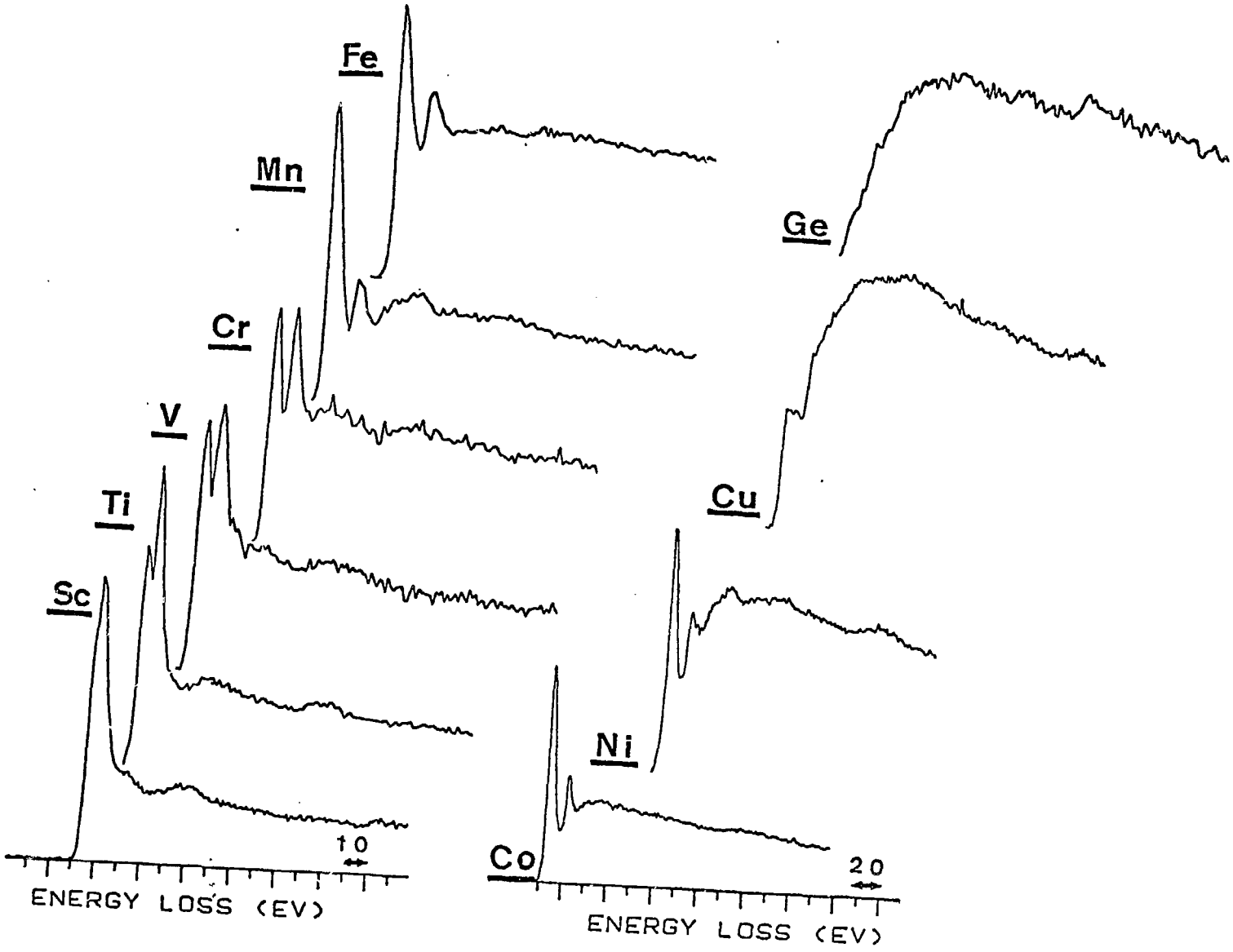
Electron Configuration: $1s^2\ 2s^2\ p^2$

Atomic Energy Levels : K-shell (1s) 283.8




K
Ca
Co
Zn
Ti
V
Cr
E (eV)
E (eV)


Nb
Mo
Ag
E (eV)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Cr
V
Ti
Sc
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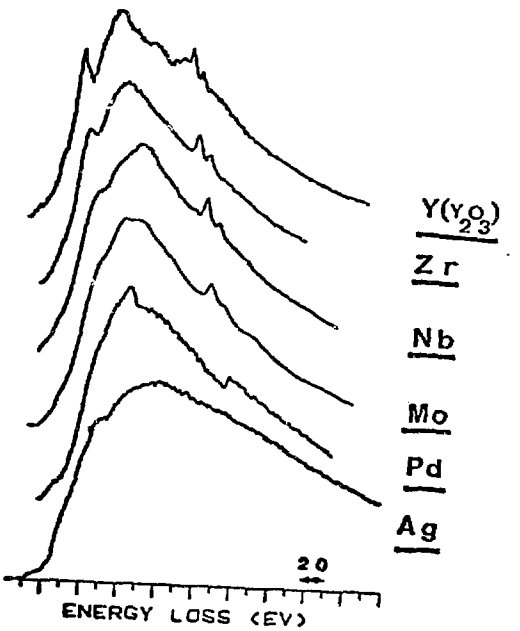
ENERGY LOSS (EV)
Ge
Cu
Ni
Co
20
ENERGY LOSS (EV)



Zaluzec figure 3b