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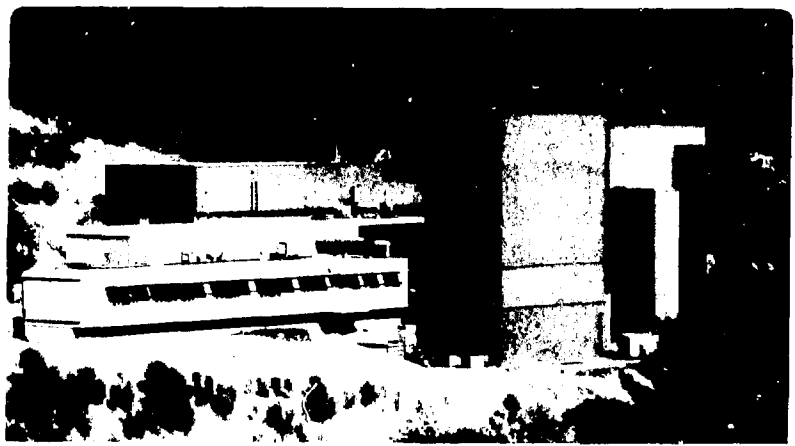
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DISCLAIMER

MEASUREMENTS OF IONIZATION CROSS-SECTIONS FOR ELECTRON ENERGY-LOSS MICROANALYSIS UNDER WELL DEFINED SCATTERING CONDITIONS

Kannan M. Krishnan and C. J. Echer

Partial cross-sections required for electron energy-loss microanalysis have been measured for a series of high purity single crystal standards. For each sample four different scattering geometries were used. The experimental data were compared with theoretical calculations using both standard hydrogenic model and parametrized Hartree-Slater cross-sections. Best agreement between theory and experiment were observed for experiments performed in diffraction mode (image coupling) with the probe convergence angle (0.84 mrad) much smaller than the spectrometer collection angle (6.84 mrad). In addition, specimen thicknesses from the region of microanalysis were measured by convergent beam electron diffraction. Absolute cross-section based on these measurements are also currently being determined.

Introduction

Quantitative microanalysis using inner-shell ionization edges in electron energy-loss spectroscopy is straight forward and can be performed by relating the experimentally measured characteristic edge intensities (integrated over an energy window of width ΔE starting at the edge onset and a collection angle β) to the concentrations of the elements of interest through the following simple equation [1]:

$$\frac{N_a}{N_b} = \frac{I_a(\beta, \Delta E)}{I_b(\beta, \Delta E)} \frac{\sigma_b(\beta, \Delta E)}{\sigma_a(\beta, \Delta E)}$$

This method of obtaining relative concentrations of the two elements 'a' & 'b' can be carried out easily if the partial scattering cross-sections of the inner-shell edges for the same energy window and collection angle, $\sigma_a(\beta, \Delta E)$ and $\sigma_b(\beta, \Delta E)$, can either be calculated using appropriate theoretical models or measured experimentally using suitable standard specimens. In practice, the implementation of this simple quantification procedure is complicated by problems of multiple scattering (if the specimens are greater than 40-50 nm thick), channelling effects in crystalline specimens (that can be generally avoided by tilting the samples to orientations where no lower order diffraction vectors are excited), convergence of the incident probe, and lens aberration effects. The theoretical models that are normally used for the calculation of the partial cross-sections assume that the inner shell cross-sections are atomic in nature. In fact, for low Z elements a hydrogenic model is used [2] with reasonable agreement with experiment. Alternatively, an atomic model using Hartree-Slater wavefunctions for transitions of inner shell electrons to the continuum has been developed [3] and is also available in a parametrized form [4]. Even if we can carefully overcome some of the experimental difficulties mentioned earlier, it is important to acertain the accuracy of the theoretical models for various scattering geometries commonly used in experiments. Hofer [5] has carried out experimental measurements of partial cross-sections for an extensive range of elements in the periodic table. Unfortunately, most of his published data is for only one scattering geometry, i.e. image mode with $\beta = 5.9$ mrads. In this paper we present measurements complementary to Hofer's results for four different scattering geometries but, for a narrow range of elements. Single crystal standards were used and specimen thickness was accurately measured by CBED. In addition to relative cross-sections this permits us to determine absolute cross-sections. The absolute measurements will be discussed in a subsequent paper [6].

Experimental Details

All electron energy-loss measurements were recorded at 200 kV on a JEOL 200CX transmission electron microscope and a Gatan 666 parallel-detection spectrometer. Electron transparent foils of high purity single crystals of BeO, BN, SiC, Si3N4, SiO2, MgO, TiC0.95 and Y3Fe5O12, prepared by ion-milling, were used in these experiments. Care was taken to tilt the foils away from any orientations where channelling effects could affect the interpretation of the results. All spectra were recorded form regions of the sample with thicknesses less than 0.2 inelastic mean free path lengths. Data were recorded under the following scattering geometries: a) Probe convergence angle $\alpha = 0.84$ mrads, Spectrometer collection angle $\beta = 6.84$ mrads, Diffraction mode (image coupling); b) $\alpha = 0.84$ mrads, β

= 6.82 mrads, Image mode (Diffraction coupling); c) α = 3.5 mrads, β = 4.56 mrads, Diffraction mode; and d) α = 3.5 mrads, β = 50 mrads, Image mode. The convergence angle was defined by the condenser aperture(s) and the collection angle was defined either by the objective aperture(s) calibrated against a well known diffraction pattern (image mode) or the spectrometer entrance aperture radius (diffraction mode). However, the β = 50 mrads experiments were carried out in image mode with no objective aperture in the path of the electron beam. These results, interpreted in terms of relative cross-sections (all ratios with respect to C-K edge) are discussed in this paper.

Precise measurements of the sample thickness were made by convergent beam electron diffraction. The thickness of the same region of the sample, obtained in terms of the mean free path length for inelastic scattering from the electron energy-loss spectrum, was used to measure the mfp accurately. This was subsequently used to measure the thickness of the sample in regions where it was too thin to apply the CBED method effectively. These results, interpreted in terms of the absolute cross-sections will be discussed in a later paper. In addition, x-ray emission spectra from the same regions of the sample were also measured. This permits a comparison of the EELS microanalysis with energy dispersive x-ray spectroscopy using our ultra-thin window detector with experimentally measured K-factors [7].

Spectra were processed using the SLEEP program developed at the NCEM. All spectra were normalized with respect to a channel to channel gain variation spectrum to minimize any variation due to the difference in the detection efficiencies of the individual elements of the diode array. In addition, a dark current spectrum obtained under the same condition, was subtracted from each inner-shell ionization edge spectrum. For each edge, either a standard power law, AE^{-r} [8] or a log-polynomial [9,10] was used to model the background. All discussions in this paper are therefore well within the limitations of the reliability of the background subtraction models.

Results and Discussions

The results of our measurements of relative (with respect to the C-K edge) cross-sections ($K_{X/C}$) are summarized in Figures 1 and 2. A 100 eV energy window was used for the quantification of all edges. The experimental data are compared throughout with partial cross-section ratios calculated using both the hydrogenic model, i.e. the SIGMAK and SIGMAL2 programs [2], and an atomic model using Hartree-Slater wavefunctions [3,4]. To accomodate the wide range in values of $K_{X/C}$ a logrithmic scale was used in the

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plots. On such a scale, experimental error bars are well within the dimension of the data points shown in the plots.

Figure 1 is a comparison of the measurements of the K edges of Be, B, C, N, O, Mg, and Si. Of the four different scattering geometries used in this study, we observe the best agreement between the theoretical calculations (both SIGMAK and H-S) and the experimental measurements for the condition $\alpha = 0.84$ mrads, $\beta = 6.84$mrads (diffraction mode). The worst agreement is for the case $\alpha = 3.5$mrads, $\beta = 50$ mrads (image mode) with considerable deviation from the theory for Be, B and O. Comparing the results for identical scattering geometries but in the diffraction (Fig 1 A) and imaging (Fig. 1 B) modes it is clear that the SIGMAK (and H-S) values are closer to the former experimental results. It also seems evident from the data that a modest disagreement between experiment and theory exists when the convergence angle is of the same order of magnitude as the collection angle (Fig 1C), even if the experiment is performed in diffraction mode and a convergence angle correction is incorporated in the calculations. Finally, if the experiment is to be performed with appropriate sensitivity to the microstructure (i.e. image mode), it seems to be preferable (comparing Figs 1B and 1D) to define the collection angle with the use of an objective aperture. It can be argued that a large collection angle is required for accuracy in the retrieval of the single-loss profiles by the Fourier-log deconvolution procedure but for thin specimens this argument is not relevant and our earlier observation remains valid. In general, from the results shown in figure 1 we can conclude that lens-aberration effects, significant at large collection angles, need to be incorporated in the analysis. This makes it difficult for making comparisons with theory under these scattering conditions.

Our discussion of the L-edges is based on the relative cross-section (again $K_{X/C}$) measurements of four elements, i.e. Si, Ti, Fe and Y. This is shown in Figure 2 (A-D). For these four elements, the difference between the diffraction and image modes for the condition $\alpha = 0.84$ mrad & $\beta = 6.84$ mrad is <10% . Apart from the condition where the convergence and collection angles are of the same order of magnitude ($\alpha = 3.5$ mrads, $\beta = 4.56$ mrads, diffraction mode; Figure 2C), the agreement between the Hartree-Slater theory and experiment is quite good, i.e. < 20%. However, for Y, the error is considerably larger (~ 50%) throughout for all experimental conditions. This could arise from the fact that the calculations were carried out only for the L_3 edge. It may be more appropriate to calculate the contributions form the L3 and L_2 edges separately, scale them in the ratio of 2:1, and add them together.

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In conclusion, it can be stated that for EELS microanalysis of light elements ($4 < z < 14$) using K edges it is important to pay attention to the exact scattering geometry. Best agreement of currently used theoretical models with experiment is observed when the experiment is performed in diffraction mode with the collection angle substantially larger than the convergence angle. Comparisons of experiments carried out in image mode, without the use of an angle defining objective aperture, with theory (hydrogenic or Hartree - Slater) can be erroneous because of lens aberration effects. For L edges, within the limited data presented in this paper we can conclude that convergence corrections incorporated in the theory may be a source of error. Relative cross-sections of M edges, absolute cross-section measurements and comparisons with low-Z microanalysis using a well characterized ultra-thin window detector from the same set of samples were also measured. This will be discussed and presented in a subsequent paper.

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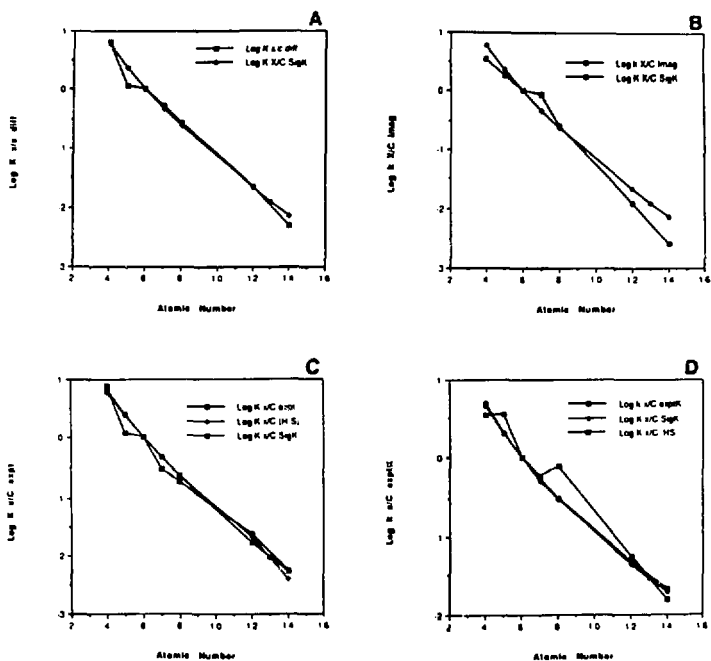
Figure 1. Experimentally measured ratios of cross-section with respect to C-K. Four different scattering geometries are shown. A) $\alpha = 0.84$ mrad, $\beta = 6.84$ mrad, diffraction mode. B) $\alpha = 0.84$ mrad, $\beta = 6.84$ mrad, image mode. In both A) and B) results from the SIGMAK program are also shown. C) $\alpha = 3.5$ mrad, $\beta = 4.56$ mrad, diffraction mode. D) $\alpha = 3.5$ mrad, $\beta = 50.0$ mrad, image mode. In both C) and D) theoretical results based on SIGMAK and Hartree-Slater parametrization are also shown for comparison.

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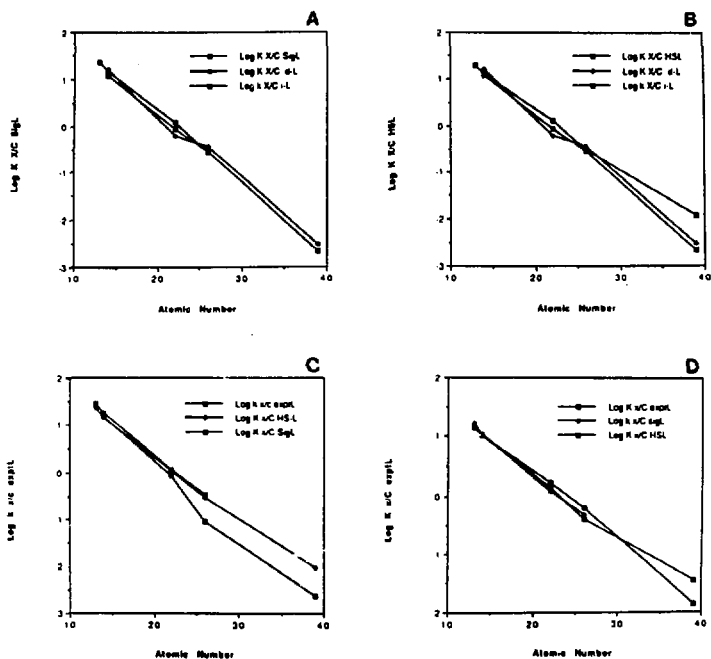
Figure 2. Experimentally measured relative cross-sections for L edges (normalized with respect to the C K edge). A) Comparison of SIGMAL2 with both diffraction and imaging modes for $\alpha = 0.84$ mrad & $\beta = 6.84$ mrad . B) Comparison of Hartree-Slater calculations with both diffraction and imaging modes for $\alpha = 0.84$ mrad & $\beta = 6.84$ mrad. C) $\alpha = 3.5$ mrad & $\beta = 4.56$ mrad, diffraction mode and D) $\alpha = 3.5$ mrad & $\beta = 50.0$ mrad, image mode. In both C) and D) the experimental results are compared with the SIGMAL2 and Hartree-Slater results.