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Measurements of absolute cross sections for K-shell ionization of Fe and Mn by electron impact

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Abstract

K-shell ionization cross sections of iron and manganese have been measured for incident electrons with energies varying in the interval from 6.5 to 40 keV, in 1 keV steps. Cross sections were obtained by measuring characteristic x-rays emitted from thin films of the elements studied deposited on carbon self-supporting backing films. Relative cross sections were obtained with uncertainties ∼3%. Transformation to absolute units increases the uncertainties to about 11%. The results are compared with those from experiments done by other groups, from various calculations based on the first Born approximation (with corrections for exchange, Coulomb and relativistic effects) and from applying a widely used semi-empirical formula.

1. Introduction

Accurate cross sections for K-shell ionization by impact of keV electrons are required for many applications, particularly for electron probe microanalysis (EPMA). Unfortunately, a systematic method for calculating ionization cross sections from first principles remains to be formulated. Calculations within the plane-wave Born approximation (PWBA) give the correct behaviour at asymptotically high incident electron energies (see e.g. Powell (1985)). Near the ionization threshold, however, the PWBA is unsuitable due to the distortion caused by the atomic field of the incident and emerging waves and because of the effect of exchange scattering. A number of semi-empirical modifications of the PWBA have been proposed to account for the above-mentioned effects (e.g. Mayol and Salvat (1990), Hippler (1990)). A more appropriate approach is to use the distorted-wave Born approximation (DWBA), in which

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the initial and final projectile wavefunctions include the distortion caused by the atomic field, because it allows a consistent description of exchange effects. Very recently, Segui (2000) and Segui *et al* (2002) developed a computer code for calculating ionization cross sections for neutral atoms using the DWBA; this approximation poses several numerical problems in the energy range considered, because of the very slow convergence of the partial-wave series. Moreover, empirical and semi-empirical cross section formulae have also been proposed (see e.g. Powell (1985) and references therein) and are widely used in applied work.

The experimental measurement of the cross section for K-shell ionization by electron impact has been a subject of continuing investigations for several decades and the available experimental data are now fairly extensive (see the recent compilations by Liu *et al* (2000) and Joy (2001)). However, close inspection of these experimental data reveals that they are scarce for many elements and, when they are available, one usually finds significant discrepancies between data from different—and even the same—laboratories. These discrepancies, which are often larger than the claimed uncertainties, make it difficult to assess the reliability of calculated cross sections over a consistent range of elements and incident electron energies. Moreover, as the number of available published data is limited, it is very difficult to judge their intrinsic accuracy. As a consequence, additional precise measurements of ionization cross sections are needed, both to confirm previous measurements and to extend the body of validated data, which is a prerequisite for improvement of practical analytical techniques such as standardless EPMA.

The measurement of absolute cross sections faces considerable difficulties. In the case of x-ray measurements on solid targets, electron transport within the active film produces a spread of the beam in energy and direction. This spread depends on the incident electron energy and, therefore, it affects not only the absolute value of the measured cross section but also the 'shape' of the cross section versus energy curve. For this reason, reliable measurements require the use of very thin, self-supporting films of the element of interest. In practice, owing to the fineness of the required films, isolated films cannot support themselves and must be deposited on a backing material, usually self-supporting thin carbon films, which are suitable due to their low atomic number and large tensile strength. Consequently, electron backscattering from the backing material further obscures the measurement, especially when a thick backing slab is used (Luo *et al* 1996). Other factors that contribute to the uncertainties in the cross section shape (relative uncertainties) are the low x-ray yield and thickness inhomogeneities which both arise from the extremely small film thicknesses. The transformation of the measured signal into absolute cross sections requires accurate and reliable knowledge of the target thickness, detector efficiency, solid angle of detection, number of incident electrons, fluorescence yield and line fractions (if only one peak is measured). These quantities are nearly independent of the incident electron energy and, therefore, systematic errors in the adopted values cause a global shift (by a constant factor) of the cross section versus energy curve without altering its shape. Another approach, which avoids the need to determine many of the above-mentioned parameters, is to consider calculated and experimental bremsstrahlung cross sections (Quarles and Semaan 1982).

In a previous work (Llovet *et al* 2000), we described an experimental method for determining K-shell ionization cross sections and reported measurements for Cu, Ni and Cr. Although absolute uncertainties were estimated at $\sim$10–12%, the shape of the cross section was obtained to an error of $\sim$2% which allowed us to show that the Mayol–Salvat and Hippler PWBA calculations satisfactorily predict (within 5%) the energy dependence of the cross section. Unfortunately, at that time the distorted-wave calculations of Segui *et al* (2002) were not available. In this work, we report on new measurements of K-shell ionization cross sections for Fe and Mn using the same experimental method, which has

been slightly improved. Fe and Mn were chosen because only data from one laboratory are available together with impact energies only up to ∼25 keV. The purpose of the present work is thus, firstly, to report new, precise experimental data for K-shell ionization cross sections for elements Fe and Mn and, secondly, to experimentally further confirm the validity of the DWBA-based calculations of Segui *et al* (2002). The experimental validation of this calculation is of great interest since the DWBA is useful for describing ionization of L and M shells, for which the available experimental data are very scarce. We also compare our measured cross sections with experimental data from other authors and from two PWBA calculations, as well as from applying the semi-empirical formula of Casnati *et al* (1982), widely used in practical applications.

2. Experimental method

The experimental technique is described in detail in Llovet *et al* (2000). Briefly, it consists of measuring the x-ray intensity N_{K} emitted from a self-supporting film of thickness t of the active element bombarded with N_{e} electrons of energy E. The K-shell ionization cross section is then obtained as

$$\sigma_{\mathrm{K}}(E) = \frac{1}{\omega_{\mathrm{K}}} \frac{I_\alpha + I_\beta}{I_\alpha} \frac{4\pi}{\mathcal{N} t N_{\mathrm{e}} \epsilon\, \Delta\Omega} N_{\mathrm{K}}(E), \tag{1}$$

where I_α and I_β are the line fractions of the Kα and Kβ peaks, $\mathcal{N}$ is the density of atoms in the target (atoms per unit volume), ω_{K} is the fluorescence yield, $\Delta\Omega$ is the solid angle of collection and ϵ is the spectrometer efficiency.

Thin Fe and Mn targets were prepared by vacuum evaporation onto self-supporting ∼30 nm thick carbon films. During the same evaporation runs, twin films of the element studied were deposited on thick polished ultra-pure GaAs and Si targets, which were used for thickness determination (see below). Targets were examined by scanning electron microscopy and those that showed appreciable islanding were rejected. Films thicknesses were obtained by measuring the ratios of the Fe Lα, Mn Kα, Ga Lα, As Lα and Si Kα x-ray line intensities for emission from the bi-layer samples considered (Fe/GaAs, Fe/Si, Mn/GaAs and Mn/Si) to those for bulk standards of the corresponding elements (the so-called k-ratios), from 4 keV up to 25 keV (see e.g. Scott *et al* (1995)). For the elements in each bi-layer, the variation of the k-ratio with incident electron energy was input to the X-FILM code of Merlet (1995). This program calculates the thickness and composition of a film on a substrate by least-squares fitting the experimental k-ratios to an analytical x-ray emission model. It is worth noticing that measurements for the substrate are not strictly necessary, but they help to verify the consistency of the results. Moreover, when the atomic numbers of the overlayer and substrate are similar, as in the present cases, the accuracy of the thickness estimation is optimal. The resulting thicknesses were in the range ∼1.2–18.9 nm, with uncertainties ranging from 1.3 to 5%. To account for the spread of the beam within the active film, the film thickness t in equation (1) was increased by an amount equal to the excess track length of transmitted electrons, estimated as described in Llovet *et al* (2000).

X-ray intensities were measured using a CAMECA SX-50 electron microprobe, from the ionization threshold up to 40 keV in 1 keV steps (0.5 keV near the ionization threshold). These measurements were done using a wavelength-dispersive spectrometer equipped with LiF and PET crystals, which was preferred to the energy-dispersive Si(Li) detector because of its higher peak-to-background ratio. Electron currents were selected to achieve a certain compromise between x-ray counting rate and film damage, with values typically of 100 nA. X-ray measurements were performed on the wavelength channel corresponding to the maximum

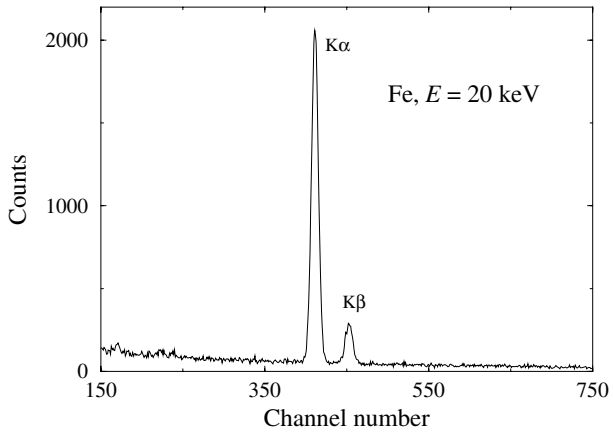

Figure 1. The x-ray spectrum of a 3.8 nm thick self-supporting Fe film at 20 keV incident electron energy, obtained with the Si(Li) detector.

of the characteristic peak and background was subtracted by linear interpolation of x-ray measurements on channels on both sides of the peak. For each element, the thinnest sample was selected. For each sample and each beam energy, at least ten measurements were performed at different positions on the sample, with counting times typically of 100 s in each position. Therefore, the standard deviation for the set of measurements not only accounts for uncertainties due to counting statistics, but also for errors arising from possible inhomogeneities in the active film thickness.

In order to convert measured x-ray intensities into absolute units (photons per incident electron and per unit solid angle) which involve the product of the detector efficiency, solid angle of collection and number of incident electrons, a series of measurements at 20 keV were performed using the Si(Li) detector, for which the efficiency and solid angle of detection can be estimated with satisfactory accuracy (see e.g. Llovet *et al* (2000)). For each element analysed, x-ray measurements were performed on samples of different thicknesses (figure 1). The linearity of the x-ray intensity with sample thickness was used as a further test of sample quality. Figure 2(*a*) shows the Mn Kα x-ray intensity yielded by selected Mn samples, at 20 keV, as a function of sample thickness. An acceptable linear relationship between the two magnitudes is exhibited, from which the corrected value of the intensity for zero thickness can be inferred. Care was taken in minimizing radiation (x-rays and electrons) originating from the interaction of incident and transmitted electrons with the specimen chamber and the supporting grid. Indeed, the emerging photon beam was collimated with a diaphragm placed in front of the detector window and an electron-absorbing device was placed below the target, aligned along the impact point of incident electrons. For each element, absolute cross sections were therefore determined from the Si(Li) x-ray measurements for samples with different thicknesses by using equation (1). The number of incident electrons N_e was evaluated by multiplying the target current I_0 by the counting time. The reliability of the 'absolute' calibration of our measurements was checked, within an error of $\sim$6%, by comparing absolute Si(Li) x-ray spectra acquired with thick targets with the results of Monte Carlo simulation, using the PENELOPE subroutine package (Acosta *et al* 1998). The final cross section value was obtained from the linear regression of the measured cross sections extrapolated to zero thickness (see figure 2(*b*)).

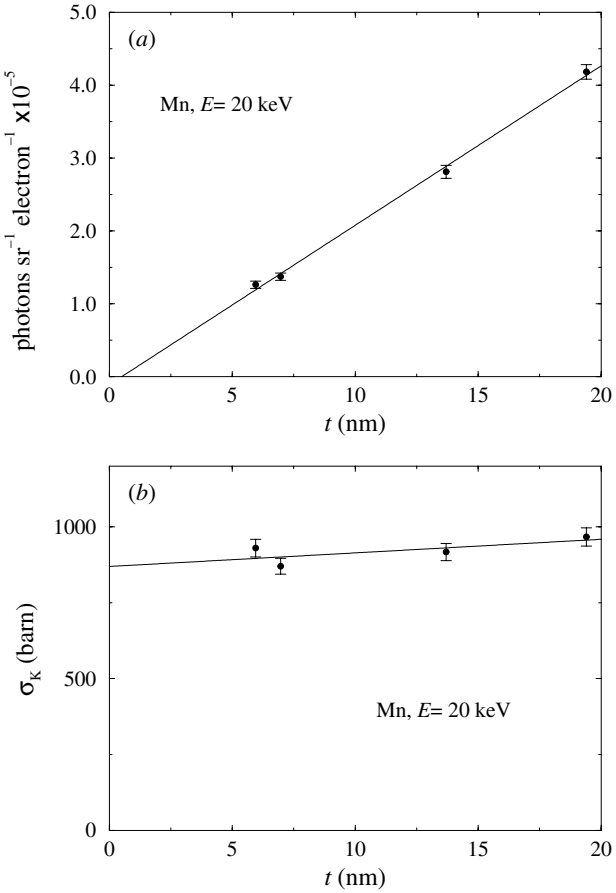

Figure 2. X-ray intensities (*a*) and measured cross sections (*b*) at 20 keV incident electron energy for selected Mn samples, as a function of sample thickness. Symbols represent measurements; continuous curves are the result of linear regression to the data. Error bars represent 1 s.d. relative uncertainties.

Relative cross sections measured with the WDS were fitted with the following analytical formula:

$$\sigma_{\mathrm{K}}(E) = C(a_1 + E^{-1})E^{-a_2}\ln(E), \tag{2}$$

where E is the incident electron energy in keV, a_1 and a_2 are free parameters and C is a normalization constant (figure 3). The parameter values obtained for Mn were $a_1 = -3.450$ and $a_2 = 0.967$, while for Fe they were $a_1 = -1.316$ and $a_2 = 1.069$. The resulting curve was scaled so as to match the absolute cross section value obtained from the Si(Li) measurements. In this way, the influence of the fluctuations in cross section shape on the scaling procedure is minimized. The appropriateness of the fit is shown in figure 3, where experimental data and fitted functions are plotted together. We see that the measurement of x-ray intensities in short steps, of 1 keV or less, leaves practically no doubt that the analytical form adopted is appropriate.

Fluorescence yields ω_{K} were taken from the recent review by Hubbell *et al* (1994). For the elements of interest, they have uncertainties of about 2–3%. The adopted values of the line fractions I_α and I_β are the most probable values reported by Khan and Karimi (1980), which were derived from a compilation of available experimental data and which are found to agree

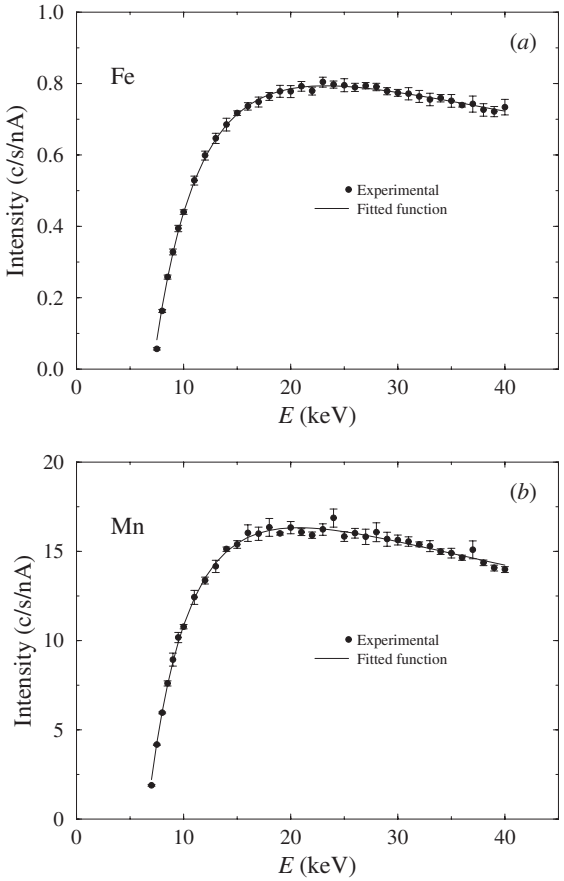

Figure 3. Measured x-ray intensity versus electron incident energy for selected (*a*) Fe and (*b*) Mn samples. Symbols represent experimental measurements. The full curve is the function given by equation (2).

satisfactorily (within less than 2%) with the line fractions observed for our measured spectra. Explicitly, the values used in the present work are the following:

$$\text{for Fe,} \qquad \omega_K = 0.351, \qquad [I(\alpha) + I(\beta)]/I(\alpha) = 1.134.$$
$$\text{for Mn,} \qquad \omega_K = 0.319, \qquad [I(\alpha) + I(\beta)]/I(\alpha) = 1.134.$$

Relative uncertainties at one standard deviation (1 s.d.) level (which include counting statistics, sample inhomogeneity, spectral background estimation and instrument drift during measurement) ranged from 0.5 to 4% for Mn (average of 2%) and 0.7 to 3% for Fe (average of 1.9%). Systematic errors were estimated to be 9.8%, which include uncertainties in the determination of the film thickness (1.3–5.4%), absolute calibration of the instrument (6%), the scaling procedure (1.7–4.3%), fluorescence yields (2–3%) and line fractions (2%). The global uncertainties, obtained by combining relative uncertainties and systematic errors in quadrature, were estimated to be ∼11%.

Table 1. Measured absolute K-shell ionization cross sections for Fe and Mn. The absolute uncertainties are about 10%.

Energy (keV)	Fe cross section (b)	Mn cross section (b)
7		101
7.5	47	222
8	136	317
8.5	216	405
9	274	476
9.5	330	542
10	368	574
11	442	662
12	500	713
13	541	755
14	573	806
15	600	820
16	616	854
17	626	852
18	639	871
19	651	853
20	650	869
21	663	857
22	652	848
23	673	865
24	667	899
25	665	843
26	660	857
27	664	836
28	661	857
29	651	836
30	647	833
31	646	829
32	639	820
33	632	815
34	635	799
35	629	794
36	619	781
37	621	804
38	608	765
39	604	750
40	614	745

3. Results and discussion

The results of our measurements are given in table 1. As mentioned above, the associated global uncertainties are of the order of 11%. Notice, however, that the shape of the cross section curve (i.e. the relative cross section values) is much more accurate ($\sim$3%), since it is only affected by relative uncertainties.

In what follows, we compare our results with the predictions of various theoretical models. The first is the plane-wave Born calculation described by Hippler (1990), in which the generalized oscillator strength is evaluated by using a hydrogenic model and simple Coulomb and exchange corrections are included. The second is a similar model proposed by Mayol

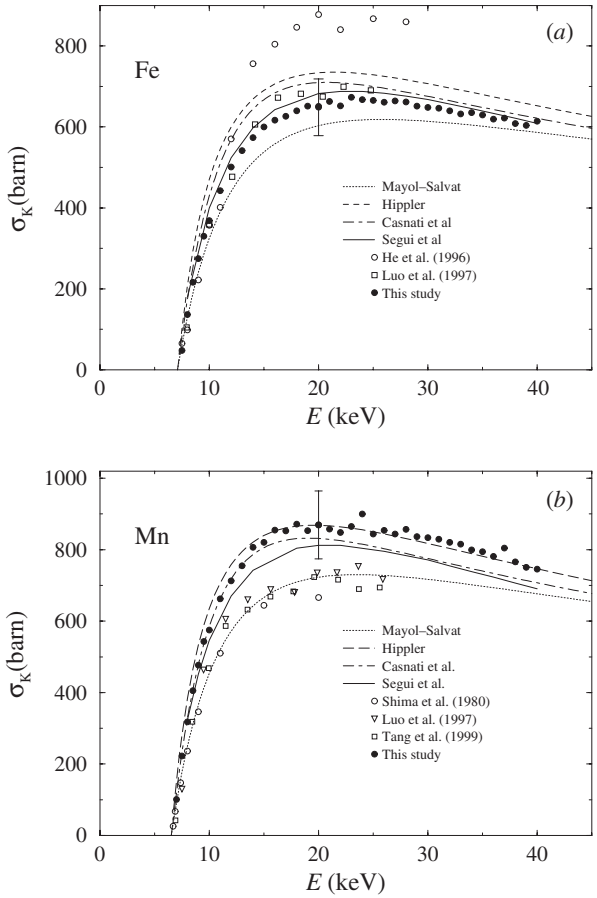

Figure 4. K-shell ionization cross section versus incident electron energy for (*a*) Fe and (*b*) Mn. The dashed curves indicate the calculation results from Mayol and Salvat's (1990) model; long-dashed curves indicate calculations according to Hippler's (1990) model; dot–dashed curves indicate the formula of Casnati *et al* (1982); full curves represent the distorted-wave calculation of Segui *et al* (2002). Full circles show results from the present measurements. Other symbols represent measurements by the authors indicated in the keys.

and Salvat (1990), which is based on a simple representation of the generalized oscillator strength obtained from the (dipole) cross section for photoelectric absorption of photons in the atomic shell considered. This model also incorporates exchange corrections, through the Ochkur approximation, and an empirical Coulomb correction. The third theoretical approach considered is the recent distorted-wave calculation of Segui *et al* (2002). Finally, we also compare our results with those obtained by applying the semi-empirical cross section formula of Casnati *et al* (1982), widely used for many applications.

Figure 4 displays our experimental results, the analytical formula of Casnati *et al* (1982), and numerical calculations of Mayol and Salvat (1990), Hippler (1990) and Segui *et al* (2002), as well as experimental data from other authors. For Fe (figure 4(*a*)), our results are in relatively good agreement with those of Luo *et al* (1997); the results of He *et al* (1996) are about 30% larger. Here our data lie between the calculations of Segui *et al* (2002) and the Mayol–Salvat model, although a slightly better agreement is found with the former calculation. In the case of

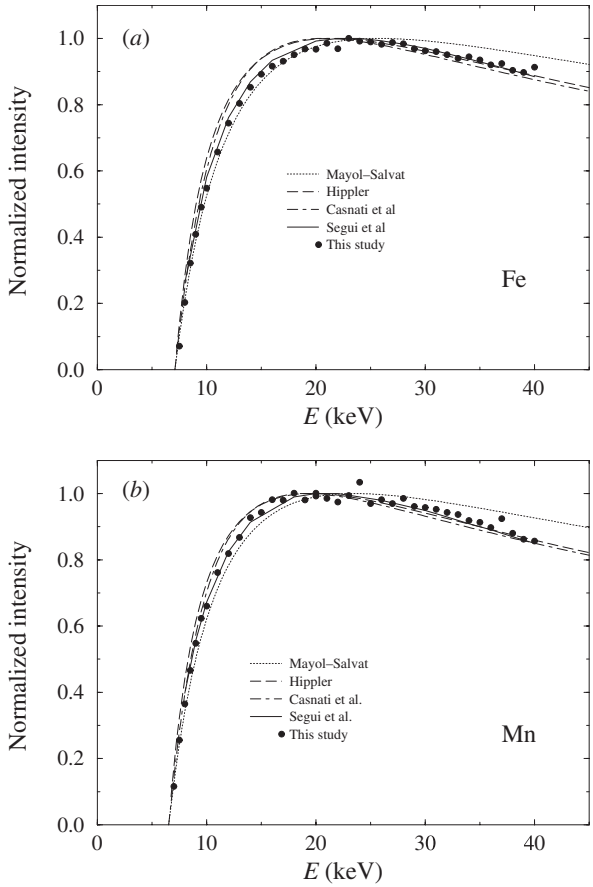

Figure 5. Experimental relative cross sections and calculated ionization cross sections (normalized to unit maximum value) for (*a*) Fe and (*b*) Mn as a function of the incident electron energy. The dashed curves indicate the calculation results from Mayol and Salvat's (1990) model; long-dashed curves indicate calculations according to Hippler's (1990) model; dot–dashed curves indicate the formula of Casnati *et al* (1982); full curves represent the distorted-wave calculation of Segui *et al* (2002). Full circles show results from the present measurements.

Mn (figure 4(*b*)), our results (solid circles) are in relatively good agreement with Hippler's theoretical model, while those of Shima (1980), Luo *et al* (1997) and Tang *et al* (1999) seem to agree more closely with the Mayol–Salvat model. Although somewhat obscured by the absolute uncertainties of our data, the agreement with the results from the DWBA calculations of Segui *et al* (2002) and Casnati *et al* (1982) is considered satisfactory. For both elements, the cross sections obtained from the formula of Casnati *et al* (1982) seem to match the distorted-wave calculation at moderately high energies, while for energies below the maximum of the cross section curve the differences between the formula and the results increase with decreasing energy.

Although comparison of cross sections in absolute units is the most stringent test of the theory, relative cross sections are affected by much smaller uncertainties and are useful in assessing the reliability of calculated cross sections. Moreover, for some applications such as EPMA, accurate knowledge of the energy dependence of the cross section is of great importance, since the technique is mainly based on ratios of quantities involving cross sections and therefore absolute values are not very relevant. In figure 5, experimental data and the theoretical curves are

rescaled, with their maximum values set to unity, to reveal differences in 'shape'. For both Fe and Mn (figures 5(*a*) and (*b*)) our experimental results are found to agree very closely with the results of the DWBA of Segui *et al* (2002), for all incident energies, although the results for Mn are obscured by the somewhat larger relative uncertainties. At low energies (below the cross section maxima) they also agree in shape with the model of Mayol and Salvat, while above the maxima the agreement with Hippler's theory and the Casnati formula seems to be better.

Our measurements for Cr, Ni and Cu (Llovet *et al* 2000) are also found to be in excellent agreement as regards shape with the distorted-wave calculations and in reasonable agreement, within the experimental error, in absolute units. These measurements have also been found to agree satisfactorily with the formula of Casnati *et al* (1982), which is in accordance with other studies (An *et al* 2000).

4. Conclusions

We have presented new measurements of K-shell ionization cross sections of Fe and Mn for electrons with kinetic energies varying from threshold up to 40 keV in steps of 1 keV or less. This near-threshold region is important in assessing the reliability of theoretical models. A significant result from the present study is the good agreement between our measured data and the DWBA calculations of Segui and collaborators. The experimental validation of this calculation method is of interest since the DWBA is a theoretical approach suitable for describing ionization in L and M shells, for which the available experimental data are very scarce. However, the numerical calculation of the DWBA cross section for these shells posess considerable numerical problems due to the low convergence rate of the partial-wave expansion of the free states. Work along these lines is currently in progress.

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