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Calculated absolute cross sections for the electron-impact ionization of the lanthanide atoms using the Deutsch-Märk (DM) formalism

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Abstract

We report results of the calculation of electron-impact ionization cross section for the lanthanide atoms Ce through Lu, which are collectively referred to as the (4f) transition-metals, using the Deutsch-Märk (DM) formalism. The lanthanides are characterized by an unfilled (5d) sub-shell and a partially filled (4f) sub-shell. The strong correlation of the open (4f) sub-shell with the (5d) sub-shell and the considerable uncertainty in the binding energies of the electrons in the (4f), (5s), (5p), (5d), and (6s) sub-shells as well as in their energetic ordering are shown to affect the choice of parameters that are required for the cross section calculations in the DM model as inferred from a comparison between the calculated DM cross sections and available experimental cross section data.

Keywords: Electron-impact ionization; Lanthanide; Cross section calculation

1. Introduction

The lanthanide atoms Ce (atomic number $Z=58$) through Lu ($Z=71$) are collectively referred to as the (4f) transition-metal atoms. In the periodic table, the lanthanides are preceded by the Ba atom, whose ground-state electron configuration is given by $\ldots 4(d)^{10}(5s)^2(5p)^6(6s)^2$. The elements Ce ($Z=58$) through Yb ($Z=70$) are characterized by an unfilled (5d) sub-shell and a partially filled (4f) sub-shell (ranging from $(5d)^0(4f)^2$ for Ce to $(5d)^0(4f)^{14}$ for Yb). Gd ($Z=64$), Tb ($Z=65$), and Lu ($Z=71$) have also a partially filled (5d) atomic sub-shell. Due to their electronic configurations, the lanthanide atoms tend to loose the $(5d)^1$ and $(6s)^2$ electrons and are most often found as triply charged cations with little or no covalent bonding. Cerium can also exist in the oxidation state +4. This feature is exploited in the use of CeO_2 as a catalyst to oxidize exhaust gases. Europium is also found as a divalent cation.

All lanthanides are chemically similar to each other. This feature can be explained by the fact that the 4f sub-shell lies inside the closed the $(5s)^2$ and $(5p)^6$ sub-shells. The so-called lanthanide contraction is the effect that the ionic radii of the lanthanides decrease through the series, from 1.16 Å (La^{3+}) to 1.03 Å (Lu^{3+}). A secondary effect is the so-called S-shape behavior. This denotes the observation that many physical properties of lanthanides, for example the hydration energies of their ions, do not change regularly with the nucleic charge. Rather, they exhibit a linear change from La to the middle of the series and then again a linear, but displaced change, up to Lu. Most lanthanides are industrially used in lasers.

The electron-impact ionization of the lanthanides has not received much attention from either experiment or theory. First, the lanthanides are in the regime of high Z-atoms in the periodic table, whose ionization has not been studied in general, with the exception of Hg ($Z=80$), Pb ($Z=82$), Bi ($Z=83$) and U ($Z=92$) [1]. From an experimental point of view, the very high boiling point of these atoms renders reliable experimental electron collision studies very difficult. In fact, we are aware of

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only two papers which reported measured ionization cross sections for Eu ($Z=63$) (along with Ba) [2] and for Ce ($Z=58$), Nd ($Z=60$), Sm ($Z=62$), Eu ($Z=63$), Gd ($Z=64$), Dy ($Z=66$), Er ($Z=68$), and Yb ($Z=70$) [3]. From an atomic structure point of view, the open (4f) sub-shell undergoes strong correlations with the (5d) sub-shell, which give rise to the prominent (4f) orbital collapse [4,5]. Lastly, there is considerable uncertainty (i) in the binding energies of the electrons in the outermost sub-shells of the lanthanides (4f), (5s), (5p), (5d), and (6s) and (ii) in their energetic ordering. Both aspects affect strongly the calculation of the electron-impact ionization cross sections (see discussion below).

In this paper, we report results of the calculation of electron-impact ionization cross sections for those lanthanides for which systematic experimental data [2,3] are available using the Deutsch-Märk (DM) formalism [1,7,8]. We note that in addition to the systematic experimental studies of Yagi and Nagata [2,3], there have been earlier measurements of ionization cross sections for four lanthanides by Shimon et al. [9]. To the extent that the data reported in Ref. [9] can be compared to those in Refs. [2,3], the data of Shimon et al. [9] tend to lie higher than those of Yagi and Nagata [2,3] and appear to be less reliable because of the absolute cross section calibration method used as discussed by the authors in [9] and a broader energy distribution of the electron beam used, which impacts in particular the low-energy region of their cross sections. We also include in our calculation the element Ba and a comparison with available experimental data [2,13]. This was done to test the influence of the use of different binding energies (taken from [3,6]) on the calculated cross sections. A detailed comparison between the calculated and the measured cross sections shows that the energetic ordering of the binding energies of the outermost sub-shells of the lanthanides may affect the choice of parameters that are required for the cross section calculations.

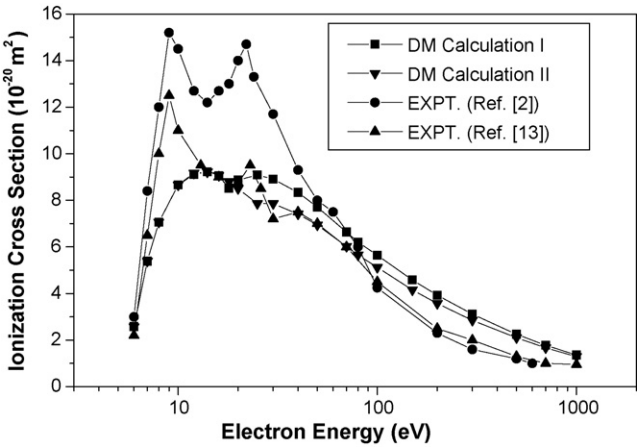

Fig. 1. Cross section for the electron impact ionization of Ba as a function of electron energy. Two DM calculations, DM Calculation I (squares, binding energies from Ref. [3]) and DM calculation II (inverted triangles, binding energies from Ref. [6]) are compared with the experimental data from Ref. [2] (circles) and from Ref. [13] (triangles).

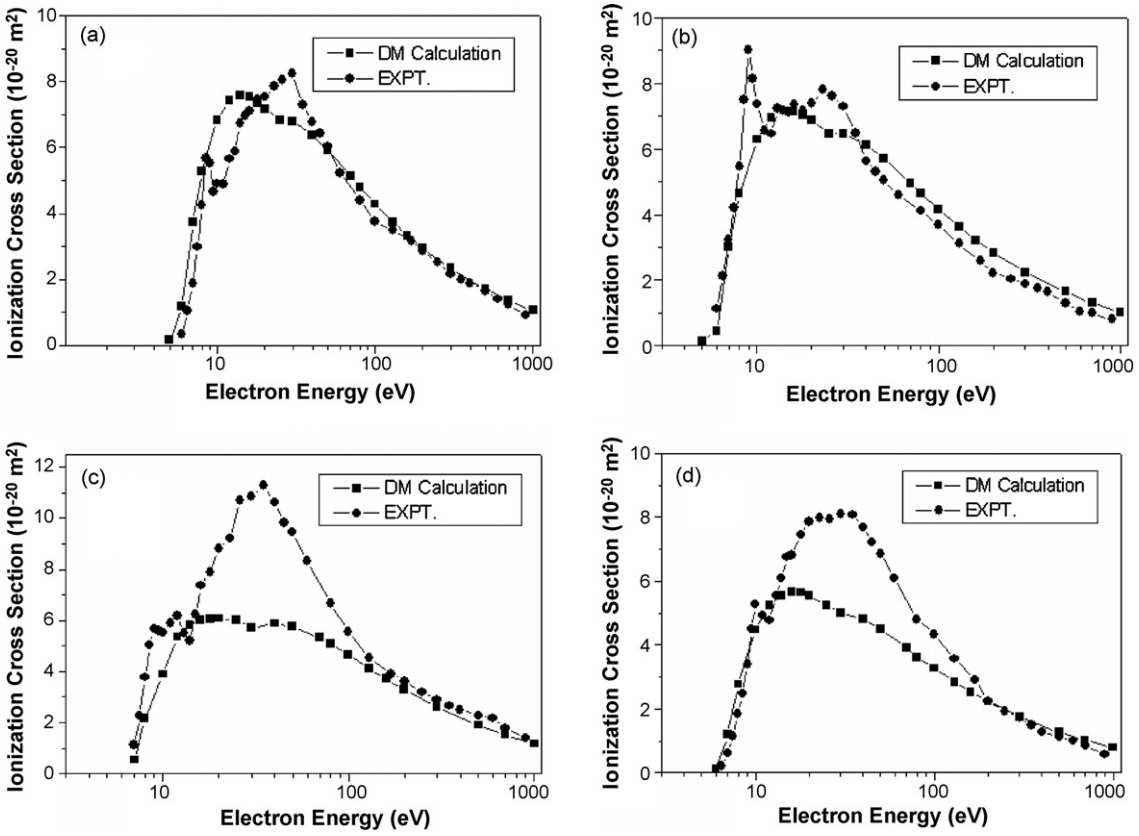

Fig. 2. Cross section as a function of electron energy for the electron impact ionization of the atoms Sm (a), Eu (b), Gd (c), and Yb (d). In all cases the present DM calculation (squares) is compared with the experimental data from Ref. [3] (circles).

2. Theoretical background

The DM formalism was originally developed for the calculation of atomic ionization cross sections and has been modified and extended several times (see e.g., Refs. [1,7,8]). The DM formula expresses the atomic ionization cross sections σ as the sum over all partial ionization cross sections corresponding to the removal of a single electron from a given atomic sub-shell labeled by the quantum numbers n and l as

$$\sigma(u) = \sum_{n,l} g_{nl}\pi r_{nl}^2 \xi_{nl} b_{nl}^{(q)}(u) \left[\frac{\ln(c_{nl}u)}{u}\right] \quad (1)$$

where r_{nl} is the radius of maximum radial density of the atomic sub-shell characterized by quantum numbers n and l (as listed in column 1 in the tables of Desclaux [10]) and ξ_{nl} is the number of electrons in that sub-shell. The sum extends over all atomic sub-shells labelled by n and l. The factors g_{nl} are weighting factors which were originally determined from a fitting procedure [11,12] using reliable experimental cross section data for the rare gases and uranium. The quantity u refers to the "reduced" energy $u = E/E_{nl}$, where E denotes the incident energy of the electrons and E_{nl} is the ionization energy in the (n, l) sub-shell. The energy-dependent function $b_{nl}^{(q)}(u)$ has the form

$$b_{nl}^{(q)} = \frac{A_1 - A_2}{1 + (u/A_3)^p} + A_2 \quad (2)$$

where the four quantities A_1, A_2, A_3, and p are constants that were determined from reliable measured cross sections for the various values of n and l [1]. The superscript "q" refers to the number of electrons in the (nl) sub-shell. The constant c_{nl} in Eq. (1) was found to be identical to one except for d-electrons.

We note that the data required for our calculations were taken from Refs. [3,6] for the case of Ba and from Ref. [3] for the lanthanides. We note specifically, that the binding energies for the outer-most sub-shells of the lanthanides given in Ref. [3] differ significantly from those given by Lotz [6].

3. Results and discussion

We start with the Ba (unfilled (5d) and (4f) sub-shells). Fig. 1 shows a comparison between our DM calculation and the experimental results reported in [2,13]. Both experimental data sets show a cross section function with two pronounced resonance structures at, respectively 9 and 22 eV, notwithstanding that there is some disagreement between the two experimental data sets in terms of the absolute magnitude of the resonance structures. With the exception of the two resonance structures (which cannot be reproduced by the DM formalism), the calculated cross section shape is in good agreement with the measured cross section function at both low and high impact energies. We note that two DM calculations were carried out for Ba using the binding energies given, respectively in [3,6]. The effect of the different sets of binding energies on the calculated cross sections is

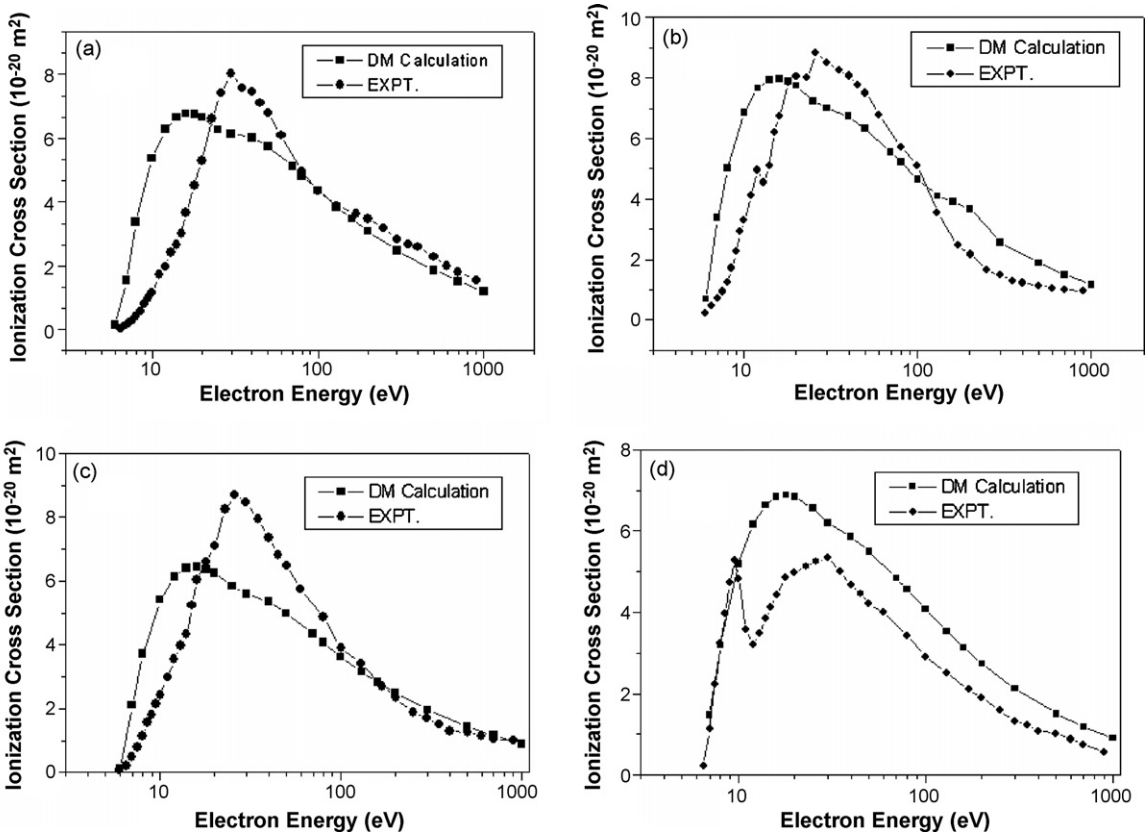

Fig. 3. Cross section as a function of electron energy for the electron impact ionization of the atoms Ce (a), Nd (b), Dy (c), and Er (d). In all cases the present DM calculation (squares) is compared with the experimental data from Ref. [3] (circles).

generally minor except for the energy region from 20 to 60 eV. The generally good agreement between measured and calculated cross section shapes at low and high impact energies indicates that the DM calculation properly represents the shape of the largest contribution to the ionization cross section, namely the shape of the cross section contribution arising from the removal of a (6s) electron.

The results for those lanthanides, for which measured cross sections are available, are shown in Figs. 2 and 3. Fig. 2 shows a comparison between measured and calculated cross sections for the four atoms Sm, Eu, Gd, and Yb. It is apparent that there is reasonable agreement in the cross section values and shapes at low and high energies (within the stated ±23% margin of error of the experimental data) for these four atoms. The region around the cross section maximum is not very well reproduced by the calculation. However, this is not surprising as this energy region is dominated by additional contributions to the ionization cross section arising from indirect ionization processes, which are not described by the DM formalism (see above for the case of Ba). For all four lanthanides shown in Fig. 2, the experimental data show a very narrow resonance peak around 9 eV and a much broader structure centered around 30 eV. In the case of the atoms Ce, Nd, Dy, and Er (Fig. 3), there is poor agreement between the DM calculation and the measured cross section at low energies and/or in the region of the cross section maximum. We note in particular the case of Er, where the DM calculation exceeds the measured cross section maxima in the region of the resonance structures (which are generally expected to increase the magnitude of the ionization cross section). Reasonably good agreement between measured and calculated cross sections is only found in the high-energy region for this second group of lanthanides. It is interesting that to note that this is the first observation of a drastic change in the low-energy shape of the measured ionization cross section with increasing atomic number Z within a row of atoms in the periodic table. It is thus not surprising that the conventional DM formalism can only reproduce the low-energy shape of the cross section functions of a few of those atoms.

In an effort to elucidate the reason(s) for this unusual finding and to address the discrepancies, we reiterate the fact stated above that the binding energies of the outermost orbitals of the lanthanides, the (4f), (5s), (5p), (6d), and (6s) orbitals, are not well known. This is particularly true for the binding energies of the (4f) orbitals where the values listed in Ref. [3] differ from the values given by Lotz [6] by as much as a factor of 3. If one calculates the ratio of E_{4f}/E_{6s} using the values given in [3], the lanthanides fall into two groups, those for which the ratio is 1.4 or less (Ce, Nd, Dy, Er) and those for which the ratio is 1.6 or larger (Sm, Eu, Gd). The low-energy shape of the ionization cross sections of the atoms in the second group (Sm, Eu, Gd, and Yb) are well reproduced by the DM formalism. One might argue that the contribution of the (4f)-electrons to the overall cross section shape is less significant here because of their comparatively large binding energy. By contrast, the lower binding energy of the (4f) electrons in the case of Ce, Nd, Dy, and Er gives rise to the unusual low-energy cross section shape for these four atoms.

In an attempt to adequately describe the energy dependence of the cross section in the case of the four atoms Ce, Nd, Dy, and Er, we tentatively described the energy dependence $b_{ns}^{(2)}(u)$ of the (6s) electrons using the constants for the principal quantum numbers $n = 1$, 2 instead of those for $n = 3$–6. This results in a cross section shape that is in very good agreement with the measured shape at low impact energies, but diverges – as one would expect – at higher impact energies. It would perhaps have been more rigorous to determine a new set of low-energy constants for the (6s) electrons from a fit to the available experimental data for the four atoms, similar to the procedure that was used to determine the original constants (see Ref. [1]). However, this procedure was deemed unreliable because of the presence of pronounced structures in the measured cross section shapes from indirect ionization processes in that energy region.

Empirically, we find that the DM formula can reproduce the cross section functions for the four atoms Ce, Nd, Dy, and Er in both the low and the high energy region, if we "split" the $f(u)$-function and use a $b_{ns}^{(2)}(u)$ function for the (6s) electrons that uses the $n = 1$, 2 constants at low energies up to $u = 4.75$ and those for $n = 3$–6 at energies above $u = 4.75$. It is not surprising that the "cross-over" between the two representations of the contributions of the (6s) electrons occurs at the same reduced energy for

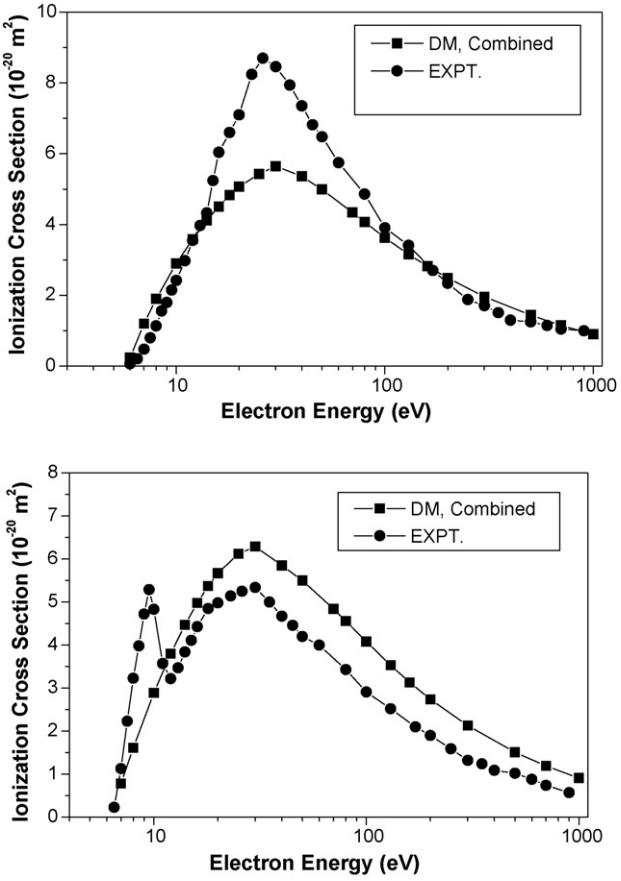

Fig. 4. Cross section as a function of electron energy for the electron impact ionization of the atoms Dy (top diagram) and Er (bottom diagram). In both cases, the modified, i.e., "combined" DM calculation (see text for details) (squares) is compared with the experimental data from Ref. [3] (circles).

all four atoms given the similarity in the ratio of the (4f) to the (6s) binding energies for these four atoms. It is also not surprising that this "cross-over" occurs near the maximum in the ionization cross section functions, i.e., in the energy range $u = 4$–5. Contributions to the ionization cross section arising from the removal of a (6s) electron dominate the low-energy part of the cross section, but become less dominant at higher energies. The results of such a modified, i.e., "combined" DM cross section functions are shown in Fig. 4 for Dy and Er. In both cases, the modified DM calculation represents the experimental data quite well over the entire energy range except for the broad resonance structure in the energy range from 20 to 80 eV in the case of Dy or the narrow resonance spike between 7 and 10 eV in Er. The level of agreement between the combined DM calculations and the experimental data is equally satisfactory for Ce and Nd (not shown here).

4. Conclusions

A comparison of calculated ionization cross sections using the DM formalism with available experimentally determined cross sections for the lanthanides showed that the level of agreement between the calculated and measured cross section shapes falls into two groups.

Reasonably good agreement was found at both low and high energies for Sm, Eu, Gd, and Tb, whereas in the case of Ce, Nd, Dy, and Er, the agreement between the DM calculation and the measured cross section at low energies was poor. This was the first observation of a drastic change in the low-energy shape of the measured ionization cross section with increasing atomic number Z within a group of atoms. It was found that these two groups of lanthanide atoms are characterized by different ratios of the binding energies of the electrons in the (4f) and (6s) subshells, one group for which the ratio of E_{4f}/E_{6s} is 1.4 or less and a second group for which the ratio is 1.6 or larger. The comparatively lower binding energy of the (4f) electrons in the case of Ce, Nd, Dy, and Er ($E_{4f}/E_{6s} < 1.4$) apparently gives rise to the unusual low-energy cross section shape for these four atoms. We found that the low-energy shape of the cross sections for these four atoms Ce, Nd, Dy, and Er can be reproduced well by using a different set of constants for the energy dependence of the (6s) electrons. Furthermore, the cross section functions for these four atoms can be described well in both the low and the high energy region by using a "split" $f(u)$-function, which employs the $n = 1, 2$ constants in the $b_{ns}^{(2)}(u)$ function for the (6s) electrons at low energies up to $u = 4.75$ and those for $n = 3$–6 at energies above $u = 4.75$.

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