

MAGNESIUM AS A REPRESENTATIVE ANALYTE METAL IN AN ARGON INDUCTIVELY COUPLED PLASMA

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Abstract

The extensive collisional-radiative (CR) model for magnesium in an argon inductively coupled plasma (ICP) is used to clarify the mechanisms by which the excited states of magnesium atoms and ions are populated under various conditions in analytical zones of different ICP systems.

Introduction

During the past few years, there has been much progress in investigation of mechanisms by which analyte atoms and ions are populated in an argon ICP. Valuable results contributing to the elucidation of the population mechanisms in metallic elements have been obtained recently by Fey et al. [1], who studied instantaneous responses of line intensities to a sudden interruption of the RF power in an argon ICP. Similarly as in the works of other authors [2 – 8] a special attention was paid to the excited states in magnesium atoms and ions.

Despite a considerable effort of many authors, the obtained experimental results have not yet been explained in a consistent way and are subject to a variety of interpretations.

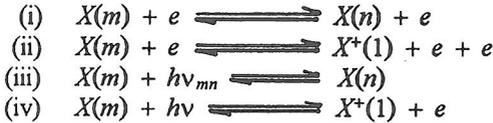
In our newest paper [9] an extensive CR model for magnesium in the argon ICP will be presented. With the help of the numerical method developed, we can calculate the population coefficients determining the populations in 29 excited effective levels of magnesium atoms and in 29 excited effective levels of magnesium ions. This enables us to study the mechanisms by which these levels are populated under various conditions in an argon ICP characterized by a set of fundamental parameters such as the electron temperature T_e , the atom temperature T_a , the electron number density n_e , the optical escape factors Λ_{mn} and Λ_m and the ground-state population of Mg atoms n_1 , Mg⁺ ions n_1^+ and Mg²⁺ ions n_1^{2+} .

The main aim of this study is to explain consistently the mechanisms populating the excited states in magnesium atoms and ions under various conditions in the analytical zones of the different ICP systems, investigated experimentally by Hasegawa and Haraguchi [2], van der Mullen et al. [3], and Burton and Blades [5].

Theoretical considerations

Our computations are based on the models of the Mg atom and Mg⁺ ion which reflect their actual structure [9]. In both cases 30 effective levels are taken into account.

The following collisional and radiative processes are considered in our version of the CR model with respect to experimentally proved effect of the charge transfer between argon and magnesium [3, 5 – 8] and to the conclusions on a negligible role of the Penning ionization [2, 6, 10] and the other inelastic collisions induced by neutral argon [10, 11]:



and



where $n = 3$ ($4s \ ^2S$) and $n = 4$ ($3d \ ^2D$), see Table 2.

Here, X and X⁺ symbolize either Mg and Mg⁺, respectively, when population mechanisms in magnesium atoms are investigated, or Mg⁺ and Mg²⁺, respectively, when populations in excited states of magnesium ions are studied.

The expressions used for the rate coefficients will be given in the paper [9]. In accordance with the literature, the electron energy distribution function is assumed to be Maxwellian [2, 10 – 12] and no radiation trapping is considered [2], i.e. $\Lambda_{mn} = 1$ and $\Lambda_m = 1$, in the ICP systems investigated.

Assuming that the quasi-stationary quasi-homogeneous state model can be applied, the solutions of the sets of coupled linear equations for unknown excited level populations n_n (Mg atom) and n_n^+ (Mg⁺ ions) can be written in the form

$$n_n = G_n^+ n_1^+ + G_n^1 n_1 \quad n = 2, \dots, 30 \quad (1)$$

and

$$n_n^+ = G_n^{2+} n_1^{2+} + G_n^{1+} n_1^+ + G_n^{CT} n_1 \quad n = 2, \dots, 30, \quad (2)$$

respectively.

Here, the population coefficients G_n^+ and G_n^{2+} characterize the respective downward recombination flows of electrons, G_n^1 and G_n^{1+} are related to the upward excitation flows of electrons from the corresponding ground states, and G_n^{CT} describes the effect of the charge transfer between Mg(1) and Ar⁺(1) on the populations n_n^+ . The inverse processes, depopulating the $4s \ ^2S$ and $3d \ ^2D$ ionic states, are included in the population coefficients G_n^{2+} , G_n^{1+} and G_n^{CT} [9].

The departures from the LTE state in the ICP systems considered here are characterized by the so-called Saha decrements $b_n = n_n/n_n^S$ and $b_n^+ = n_n^+/n_n^{+S}$, where S symbolizes the corresponding Saha values.

In order to find actual values for n_1 , n_1^+ and n_1^{2+} at various positions in an ICP the presented CR model should have to be combined with complex models for the

evaporation and transport of analytes in the argon plasma. This was done by Fey et al. [13] for lithium in the central channel of an ICP.

Present study deals with the mechanisms populating the excited states of magnesium atoms and ions in the analytical zones of the different ICP systems, where the observation heights above the load coil and the radial distances from the plasma centre were in the range from 15 to 16 mm and from 0 to 2 mm, respectively. As the transport frequency of analytes is relatively low in these positions [13], the values of b_1 in the range from 1 to 10, $b_1^+ = 1$ and $b_1^{2+} = 1$ have been used in our calculations as realistic estimations [3, 5, 13] determining the input parameters in the equations (1) and (2).

Results and discussion

In Fig. 1, 2 and 3 our numerical results for the Saha decrements are compared with the respective experiments carried out by van der Mullen et al. [3], Burton and Blades [5], and Hasegawa and Haraguchi [2] on the different ICP systems in their analytical zones.

As can be seen, our model provides a good picture of the processes determining the populating mechanism in all experimental situations investigated. The registered sensitivity of the values of n_n and n_n^+ to the value of b_1 is a natural consequence of the dominance of the excitation flow of electrons from the ground state in the population mechanisms of the Mg excited states and of the charge transfer in the population mechanisms of the Mg⁺ excited states, respectively. Only the highest levels are populated by the corresponding recombination flows from continuum in both atomic and ionic system.

Our results in Fig. 3 confirm the experiments of Hasegawa and Haraguchi [2] who found that no excited states of the magnesium ion were demonstrably overpopulated with respect to the other ionic levels due to the charge transfer. This conclusion, contrasting with the measurements of van der Mullen et al. [3], and Burton and Blades [5], is considered to be surprising in the literature (see, e.g. [5]). However, from our

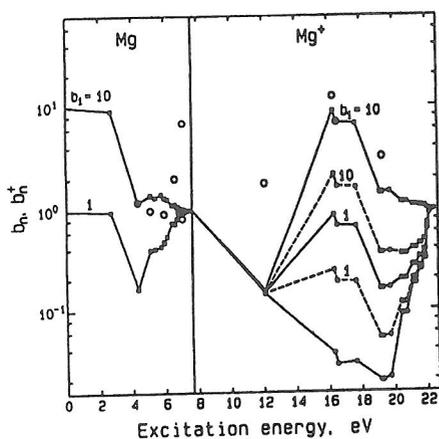


Fig. 1. The numerical results for the Saha decrements, together with the corresponding experimental values (circles) [3], obtained with the local experimental values of $T_e = 6700$ K, $n_e = 1.6 \times 10^{14} \text{ cm}^{-3}$ and with an estimated value of $T_a = 6000$ K. The results for b_n^+ : full curves (the charge transfer according to Hasted [14]), broken curves (the charge transfer according to Farnsworth and Omenetto [8]), dotted curve (without charge transfer).

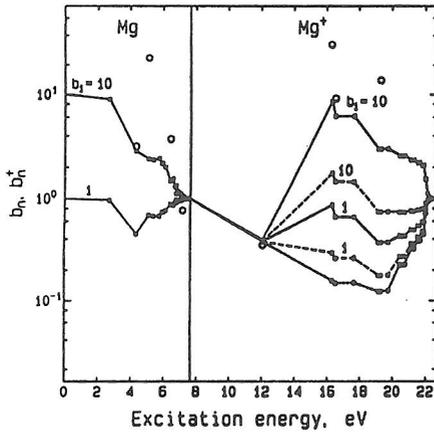


Fig. 2. As in Fig. 1, but under the conditions [5], where $T_e = 7400$ K, $n_e = 6.0 \times 10^{14} \text{ cm}^{-3}$ and $T_a = 6700$ K.

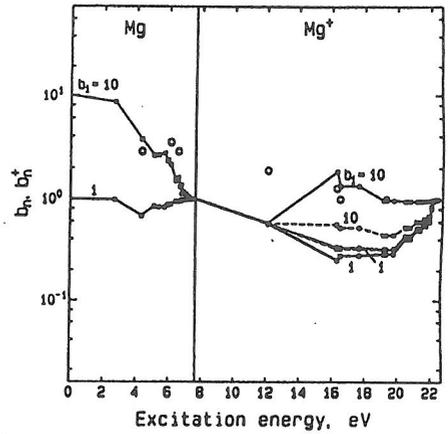


Fig. 3. As in Fig. 1, but under the conditions [2], where $T_e = 8400$ K, $n_e = 1.4 \times 10^{15} \text{ cm}^{-3}$ and $T_a = 6500$ K.

numerical analysis [9] it follows that the value of b_n^+ for the ionic levels, sensitive to the charge transfer, decreases with a growing value of T_e . In the case of Hasegawa and Haraguchi [2] the value of $T_e = 8400$ K is greater than those values determined in the works [3, 5]. Moreover, this value of T_e is greater than the corresponding LTE electron temperature, which was used instead of T_e by van der Mullen et al. [3], and Burton and Blades [5].

In spite of the fact that only reasonable estimations of b_1 , b_1^+ and b_2^+ have been used by us, the effective rate constant of $1.1 \times 10^8 \text{ s}^{-1}$ determined by Farnsworth and Omenetto [8] for the transfer of charge from Mg^+ to Ar seems to be too small (see broken curves in Fig. 1 - 3).

In Tables 1 and 2 the basic data characterizing the selected excited levels of magnesium atom and ion are given. Their population mechanisms are analysed in Tables 3 and 4.

Table 1. Data characterizing the selected excited levels of magnesium atom [9].

| Level number n | Designation | Excitation energy, ϵ_{1n} (eV) | Statistical weight, g_n |
|---------------------|--------------|--|---------------------------|
| 2 | $3p \ ^3P$ | 2.714 | 9 |
| 3 | $3p \ ^1P$ | 4.346 | 3 |
| 4 | $4s \ ^3S$ | 5.108 | 3 |
| 7 | $4p \ ^3P$ | 5.932 | 9 |
| 10 | $5s \ ^3S$ | 6.431 | 3 |
| 21 | $7s \ ^1S$ | 7.178 | 4 |
| 26 | $n_{pq} = 8$ | 7.434 | 256 |

Table 2. Data characterizing the selected excited levels of magnesium ion [9].

| Level number n | Designation | Excitation energy, ϵ_{1n} (eV) | Statistical weight, g_n |
|-------------------|-----------------|--|---------------------------|
| 2 | 3p 2P | 4.430 | 6 |
| 3 | 4s 2S | 8.655 | 2 |
| 4 | 3d 2D | 8.864 | 10 |
| 6 | 5s 2S | 11.504 | 2 |
| 8 | 4f 2F | 11.629 | 14 |
| 17 | 7p 2P | 13.664 | 6 |
| 26 | $n_{pq^n} = 10$ | 14.491 | 200 |

Table 3. The effect of the excitation flow of electrons from the ground state of magnesium atom on the populations n_n of several selected atomic levels in the analytical zones if the different ICP systems [2, 5] at $b_1 = 1$ and $b_1 = 10$.

| Level number n | $G_n^I n_1 / n_n (\%)$ | | | |
|-------------------|--|------------|--|------------|
| | $T_o = 7400\text{ K}$ $T_a = 6700\text{ K}$ $n_o = 6.0 \times 10^{14}\text{ cm}^{-3}$ (see [5]) | | $T_o = 8400\text{ K}$ $T_a = 6500\text{ K}$ $n_o = 1.4 \times 10^{15}\text{ cm}^{-3}$ (see [2]) | |
| | $b_1 = 1$ | $b_1 = 10$ | $b_1 = 1$ | $b_1 = 10$ |
| 2 | 91.9 | 99.1 | 86.6 | 98.5 |
| 3 | 60.1 | 93.8 | 49.2 | 90.6 |
| 4 | 27.9 | 79.5 | 23.6 | 75.6 |
| 7 | 21.4 | 73.2 | 18.5 | 69.4 |
| 10 | 7.6 | 45.2 | 6.9 | 42.3 |
| 21 | 1.0 | 9.2 | 0.9 | 8.3 |
| 26 | 0.1 | 1.0 | 0.1 | 0.9 |

Table 4. The effect of the excitation flow of electrons from the ground state of magnesium ion and the charge transfer between magnesium atoms and argon ions on the populations n_n^+ of several selected ionic levels in the analytical zones of the different ICP systems [2, 5] at $b_1 = 1$ and $b_1 = 10$.

| Level number n | $G_n^{I+} n_1^+ / n_n^+ (\%)$ and $G_n^{CT} n_1 / n_n^+ (\%)$ | | | | | | | |
|-------------------|--|------|------------|------|--|------|------------|------|
| | $T_o = 7400\text{ K}$ $T_a = 6700\text{ K}$ $n_o = 6.0 \times 10^{14}\text{ cm}^{-3}$ (see [5]) | | | | $T_o = 8400\text{ K}$ $T_a = 6500\text{ K}$ $n_o = 1.4 \times 10^{15}\text{ cm}^{-3}$ (see [2]) | | | |
| | $b_1 = 1$ | | $b_1 = 10$ | | $b_1 = 1$ | | $b_1 = 10$ | |
| 2 | 99.5 | 0.5 | 95.1 | 4.9 | 99.8 | 0.1 | 98.6 | 1.4 |
| 3 | 2.4 | 97.6 | 0.2 | 99.8 | 29.4 | 70.1 | 4.0 | 95.9 |
| 4 | 8.3 | 91.7 | 0.9 | 99.1 | 55.2 | 43.5 | 11.2 | 88.5 |
| 6 | 8.2 | 78.9 | 1.0 | 97.4 | 34.5 | 26.5 | 10.2 | 78.3 |
| 8 | 8.2 | 78.9 | 1.0 | 97.4 | 34.5 | 26.5 | 10.2 | 78.3 |
| 17 | 4.4 | 41.6 | 0.9 | 87.7 | 13.3 | 10.2 | 7.0 | 53.2 |
| 26 | 0.2 | 2.0 | 0.2 | 16.9 | 0.6 | 0.5 | 0.6 | 4.4 |

As it shown is in Table 3, the upward excitation flow of electrons from the ground state of the Mg atom dominates over their recombination flow in populating of many atomic excited states except for those with relatively high excitation energies (see Table 1). This conclusion is in excellent accordance with the measurements of Fey et al. [1], who observed a similar behaviour also for other elements, such as Na, Ca, Cu, Al, Cd and Fe. This can be explained by the relatively small excitation energy of their first excited states (see Table 1).

The numerical results presented in Table 4 support the conclusions of Fey et al. [1] also of Farnsworth et al. [6] and Ogilvie and Farnsworth [7], who investigated the excitation and ionization mechanisms in magnesium by means of a manipulation of the populations in atomic and ionic excited states by pulsed dye lasers [6] and correlations between intensity fluctuations in atomic and ionic emission lines [7]. As can be seen, the first excited level of Mg^+ ions is populated by the excitation from the ground state of the ion. The charge transfer between argon ions and the ground-state magnesium atoms is an important population process not only for the so-called quasi-resonant $4s^2S$ and $3d^2D$ levels (with their total excitation energies of 16.301 and 16.510 eV, respectively, close to the argon ionization limits of 15.760 and 15.937 eV), but also for those levels which are populated predominantly by electron collisions from the $4s^2S$ and $3d^2D$ states. As in the atomic system, the highest ionic levels are populated mainly by the recombination flow from continuum.

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