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INTENSITY ENHANCEMENT IN THE EMISSION SPECTRA OF Sb, Sn, AND W IONS DUE TO THE MIXING OF CONFIGURATIONS WITH SYMMETRIC EXCHANGE OF SYMMETRY

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The essential narrowing of emission spectrum due to the configuration mixing with a symmetric exchange of symmetry is considered for ions with an open $4d^N$ electron shell. The relativistic CI calculations have been performed for Sn^{9+}–Sn^{12+} and Sb^{10+}–Sb^{11+} ions, which are the most promising emitters for EUV lithography, and for W^{q+} ions, which give a strong undesirable emission in tokamak plasma. It is shown that the inclusion of interaction with other energetically neighbouring configurations only weakly influences the integral characteristics of the main group of lines or quasicontinuum band – its total intensity, width, and shape. The similarity between photoexcitation and emission spectra, related with the ground level, that has been previously established for highly charged tungsten ions, manifests itself also at medium ionization degrees. The relative widths of intense groups of lines in such spectra of tin and antimony ions increase in comparison with tungsten; however, the spectra of Sn^{9+} and Sb^{10+} with a half-filled $4d^5$ shell have an extremely narrow width.

Keywords: multicharged ions, configuration mixing, integral characteristics of spectra, EUV lithography, thermonuclear plasma

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1. Introduction

One of the strongest correlation effects in atoms is the so-called configuration mixing with a symmetric exchange of symmetry (SEOS correlations) [1, 2], when one electron is filling the vacancy in a lower shell with the same principal quantum number while the other electron is excited to an empty shell also without a change of the principal quantum number:

$$nl^{4l+1}n(l+1)^{N+1} + nl^{4l+2}n(l+1)^{N-1}n(l+2)\,. \quad (1)$$

The wave functions of these neighbouring shells strongly overlap, and thus the interconfiguration matrix elements have rather large values. On the other hand, the increase of energy of one electron compensates the decrease of energy of another electron; consequently, the distances between the levels of these configurations are rather small. Hence the both conditions of strong configuration mixing are fulfilled.

One of essential features of these configurations is that they both are related through dipole transitions with the same ground configuration $nl^{4l+2}n(l+1)^N$. For this reason such configuration mixing has a strong effect on the corresponding photoexcitation and emission spectra. In the two-configuration approximation these spectra of some ions undergo an essential narrowing with respect to the single-configuration calculation result: the most intense lines are concentrated in a narrow interval of wavelengths and the quasicontinuum band is formed [3]. Such emission spectra are considered to be useful as a source of EUV (extreme ultraviolet) radiation. Namely, the emitter with a wavelength near 13.5 nm within a narrow bandwidth is required for the development of EUV lithography (the rays of such a wavelength are effectively reflected and focused by Mo / Si multilayers) [4]. The possibility of using the transitions

$$4p^54d^{N+1} + 4p^64d^{N-1}4f \to 4p^64d^N \quad (2)$$

in the ions of xenon [5–7] and tin [7–9] was considered. For the purpose of investigating which ions are most suitable as the required source of EUV emission, the calculation of integral characteristics of these transitions for a wide interval of ionization degrees and atomic numbers around Z = 50 was performed in [10], and the ions with the optimal set of atomic characteristics were determined.

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The same transitions in the highly charged tungsten ions play a negative role, as they cause large radiation losses in tokamak plasma [11]. Tungsten due to its resistance to sputtering is used as the first wall material in a divertor and other parts of camera. However, tungsten ions can migrate to the central torus and radiate intensely there, particularly in the region of quasicontinuum band corresponding to transitions (2) at various numbers of electrons in a $4d^N$ shell. Such emission of the separate tungsten ions was investigated experimentally in an EBIT (Electron Beam Ion Trap) facility and interpreted theoretically using the collisional-radiative model [12, 13]. It was shown in [14] that in the case of a low density plasma obtained in EBIT and the contemporary tokamaks all the main features of these spectra can be reproduced using the assumption that the excitations originate only from the ground level. It enabled one to explain some main regularities of the quasicontinuum band and its satellite.

The aim of this work is to continue the theoretical investigation of these important spectra by considering the influence of some relativistic and configuration mixing effects not taken into account in [14], and to compare the main features of spectra for highly and moderately charged ions. Calculations have been performed in a relativistic CI approximation using Dirac–Fock wave functions [15] and in quasirelativistic approximation [16] as well.

2. Results and discussion

As it was shown in [10], the two-configuration approximation (1) enabled us to describe correctly the formation of a narrow group of intense lines in photoabsorption and emission spectra and to obtain rather accurate values of the main characteristics for this group of lines. Recently the probabilities of transitions (2) at N = 2 for Sn^{12+} have been calculated semiempirically, taking into account configurations $4p^6 4d\,nl$ ($n \leq 6$, $l = s, p, d, f$), $4p^5 4d^3$, $4p^6 5s^2$, $4p^5 4d^2 5s$ and scaling down various integrals to different extent [17]. These results have been used for the identification of about seventy lines in the vacuum spark spectrum. In Fig. 1 these semiempirical data are compared with the results of *ab initio* relativistic calculations in two-configuration and single-configuration approximations. In the latter case the transition probabilities of two independent arrays are distributed in a very wide interval of wavelengths and do not reproduce the semiempirical spectrum at all. When taking into account the SEOS mixing of initial configurations, the distribution of probabilities changes essentially, the lines are quenched in a large part of energy interval of the spectrum, and the transition probability is concentrated within the narrow group of intense lines. A fairly good correspondence to the semiempirical spectrum and to its integral characteristics is obtained. It is these characteristics that are important for the EUV emitter.

On the grounds of calculations of integral characteristics for transitions in two-configuration approximation using quasirelativistic wave functions the conclusion was made that from the atomic point of view the strongest emitters in the narrowest interval around 13.5 nm are ions Sn^{9+}–Sn^{11+} and Sb^{10+}–Sb^{11+} [10]. In the present work the calculation results for these ions are specific in two ways: relativistic Dirac–Fock functions are used instead of quasirelativistic wave functions and the additional integral characteristics – halfwidth of the intense group of lines and total transition probability – are given (Table 1). More accurate relativistic calculations do not change the main conclusions made in [10], but improve the values of average wavelength, which are diminished by 0.13–0.23 nm. For Sn^{12+} the obtained result corresponds better to that of semiempirical spectrum. It is necessary to note that in the present relativistic and quasirelativistic calculations the values of radial integrals are not diminished. The difference in the values of gA for both approximations is insignificant: it does not exceed 1%. The spectral interval containing some fixed percent of the total transition probability (in the vicinity of the average wavelength) as well as the halfwidth of the intense group of lines are obtained larger using the relativistic Dirac–Fock wave functions.

In the two-configuration approximation the emission spectra of tungsten ions W^{29+}–W^{34+}, excited from the ground level, were obtained to be very similar to the photoexcitation spectra from this level [14] and both types of spectra were concentrated in a very narrow interval of wavelengths. Consequently, the transitions from or to the ground level are more influenced by SEOS correlations than the other transitions. This suggests the possibility to obtain a narrow emission band using the plasma of low density in which practically only the ground level of ions is populated.

The narrowing of emission spectrum can be estimated by comparing the whole interval of spectrum ($\Delta\lambda_{\rm s}$) with the width of the main group of lines, the intensities of which exceed some percent of the most intense line ($\Delta\lambda_{\rm il}$). In the considered spectra the relative intensities of lines out of the interval of intense

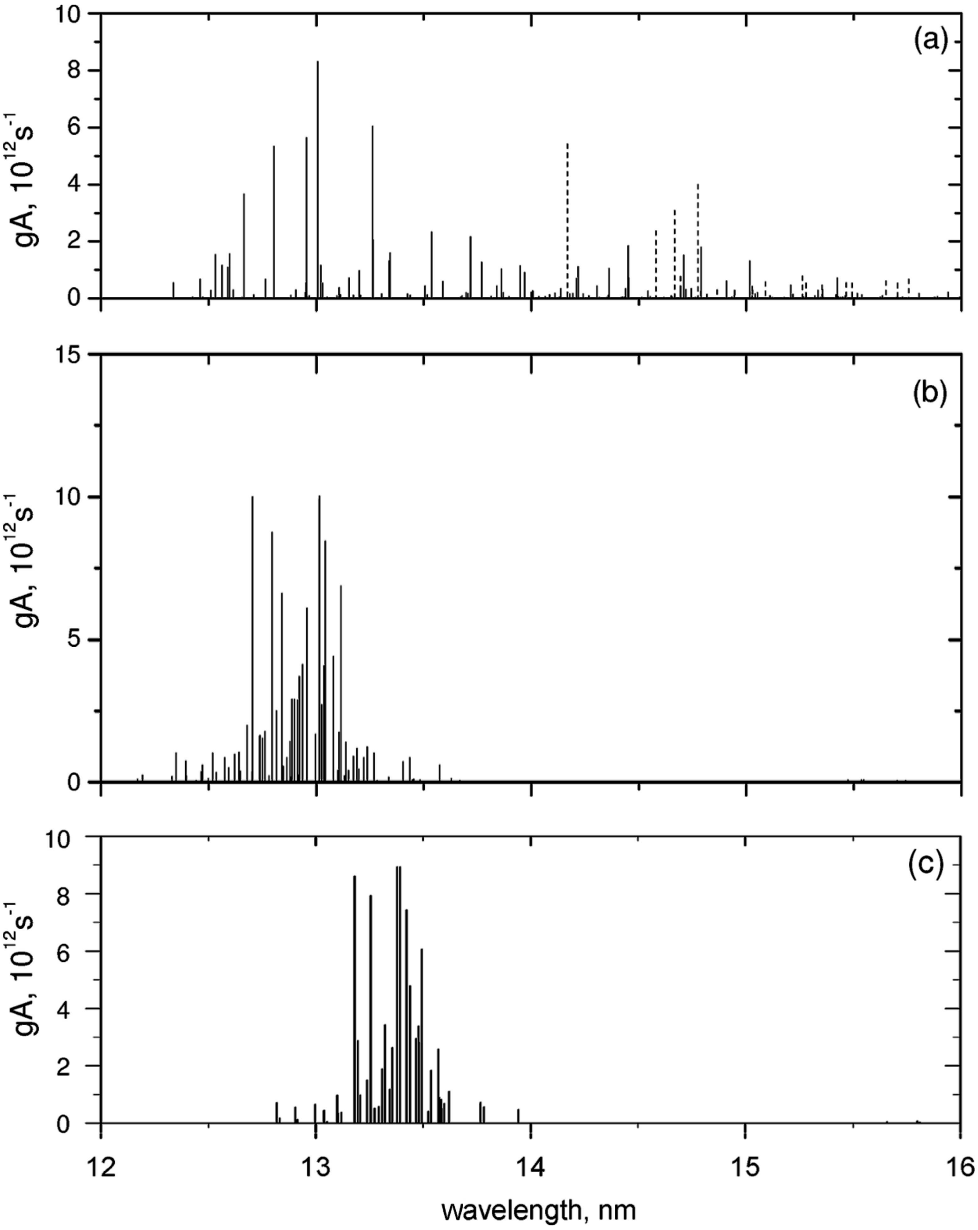

Fig. 1. Distribution of the probabilities for transitions $4p^54d^3 + 4p^64d4f \to 4p^64d^2$ in Sn^{12+} calculated in a (a) single-configuration and (b) two-configuration relativistic approximations and (c) semiempirically [17]. In (a) the solid lines correspond to the transitions $4p^54d^3 \to 4p^64d^2$, and the broken ones to the transitions $4p^64d4f \to 4p^64d^2$. From semiempirical data only the lines classified as the above indicated transitions are given.

band usually do not surpass the 5% limit, thus this value is chosen as the criterion. For the emission spectra excited from the ground level of tungsten ions W^{29+}–W^{34+} the ratio $\Delta\lambda_s/\Delta\lambda_{il}$ is of the order of 100. However, for the ions W^{35+}–W^{37+} with the number of $4d$ electrons $N \leq 3$ the intense lines are dispersed in a considerably wider interval. As explained in [14], the transitions to the open $4d^N_{3/2}$ subshell account for it. However, the splitting of shells into subshells does not manifest itself at medium ionization degrees. The abovementioned ratio for the most ions of tin does not exceed 20 (Table 2; a considerable difference between the estimated values of $\Delta\lambda_{il}$ for Sn^{10+} and Sn^{11+} in two approximations is caused by a distant line, with relative intensity slightly exceeding 5%, emerging in the relativistic approximation). As an exception, an extremely narrow spectrum is obtained for Sn^{9+} at the excitation from the ground level of the half-filled shell (Fig. 2). The intensity of emission as well as that of photoexcitation spectrum for this ion is concentrated only in four lines; both spectra are rather similar, like it is in the case of tungsten ions spectra. As seen from

Table 1. The main integral characteristics of the distribution of $(4p^5 4d^{N+1} + 4p^6 4d^{N-1} 4f) - 4p^6 4d^N$ transition probabilities for the ions Sn^{q+} and Sb^{q+} calculated in two-configuration relativistic, quasirelativistic, and empirical [17] approximations. $\Delta\lambda$ is the interval of spectrum in the vicinity of the average wavelength $\bar{\lambda}$ containing 80% and 90% of the total probability gA_{tot}.

Element	q	N	Method of calculation	$\bar{\lambda}$, nm	gA_{tot}, 10^{14} s^{-1}	$\Delta\lambda$, nm 80%	$\Delta\lambda$, nm 90%	Halfwidth
Sn	9	5	rel.	13.50	9.35	0.92	1.27	0.42
			quasirel.	13.27	9.33	0.85	1.23	0.37
	10	4	rel.	13.21	7.44	0.66	0.99	0.53
			quasirel.	13.04	7.40	0.61	0.92	0.49
	11	3	rel.	13.05	3.96	0.66	0.82	0.50
			quasirel.	12.91	3.94	0.61	0.82	0.48
	12	2	rel.	12.97	1.36	0.53	0.66	0.41
			quasirel.	12.84	1.36	0.49	0.59	0.40
			empir.	13.37	1.04	0.37	0.41	0.31
Sb	10	5	rel.	12.53	10.53	0.65	1.01	0.26
			quasirel.	12.35	10.46	0.59	0.95	0.24
	11	4	rel.	12.36	8.22	0.54	0.76	0.40
			quasirel.	12.21	8.16	0.49	0.69	0.40

Table 2. The intervals of wavelengths of the whole emission spectrum corresponding to the transitions $4p^5 4d^{N+1} + 4p^6 4d^{N-1} 4f \rightarrow 4p^6 4d^N$ ($\Delta\lambda_{\mathrm{s}}$) and of the main group of lines with intensities exceeding 5% of that of the most intense line ($\Delta\lambda_{\mathrm{il}}$). The initial levels are populated by excitation from the ground level of configuration $4p^6 4d^N$. Results of the relativistic (for W^{q+}) and quasirelativistic calculations (for Sn^{q+} and W^{q+}) in two-configuration approximation.

N	Sn^{q+} q	Sn^{q+} $\Delta\lambda_{\mathrm{s}}$, nm rel.	Sn^{q+} $\Delta\lambda_{\mathrm{s}}$, nm quasirel.	Sn^{q+} $\Delta\lambda_{\mathrm{il}}$, nm rel.	Sn^{q+} $\Delta\lambda_{\mathrm{il}}$, nm quasirel.	W^{q+} q	W^{q+} $\Delta\lambda_{\mathrm{s}}$, nm	W^{q+} $\Delta\lambda_{\mathrm{il}}$, nm
9	5	6.59	6.83	2.95	2.23	29	3.03	0.03
8	6	8.73	9.07	2.13	1.94	30	4.28	0.04
7	7	9.75	11.44	1.10	0.76	31	5.50	0.04
6	8	12.13	13.40	0.75	0.72	32	6.89	0.06
5	9	13.82	15.21	0.06	0.065	33	8.82	0.09
4	10	14.10	16.46	0.34	0.38	34	9.55	0.00
3	11	13.08	13.40	0.89	0.19	35	9.80	2.09
2	12	10.83	11.93	1.23	0.33	36	8.02	6.12
1	13	7.23	7.30	0.47	0.45	37	5.25	1.93

Table 1, the average wavelength of this narrow group of lines is close to 13.5 nm. It suggests the possibility to use the emission of Sn^{9+} in low density plasma for the purposes of EUV lithography. The similarity between the absorption and emission spectra related with the ground level manifests itself for other Sn and Sb ions as well.

From the comparison of calculated transition probabilities for Sn^{12+} with the semiempirical ones, which take into account the interaction of many excited configurations, it follows that the extension of configuration set only weakly influences the width and shape of the intense group of lines. It agrees with the conclusion made in [14] from the comparison of the emission spectra for tungsten ions. In this work the emission spectra obtained after dipole excitation from the ground level were calculated for tungsten ions using the following sets of configurations for the initial and final states:

$$4p^5 4d^{N+1} + 4p^5 4d^N 5s + 4p^6 4d^{N-1} 4f + 4p^6 4d^{N-2} 4f 5s \rightarrow 4p^6 4d^N + 4p^6 4d^{N-1} 5s \, . \quad (3)$$

The extended calculations enabled one to interpret the satellite line with an approximately constant wavelength of 4.5 nm emerging in the spectra of various

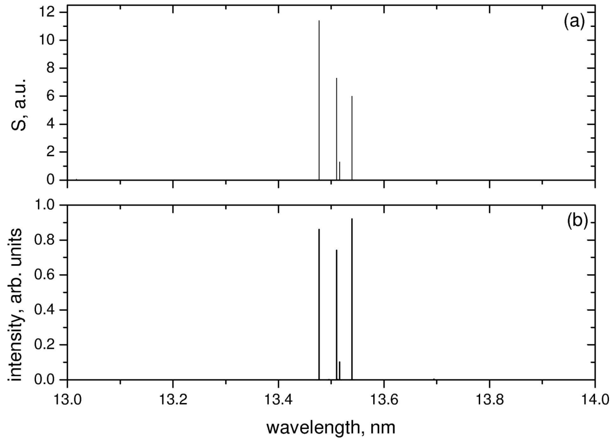

Fig. 2. (a) Photoexcitation spectrum, corresponding to the transitions $4p^64d^5 \rightarrow 4p^54d^6 + 4p^64d^44f$ from the ground level, and (b) in this way excited emission spectrum $4p^54d^6 + 4p^64d^44f \rightarrow 4p^64d^5$ for Sn^{9+}. Results of calculation in a relativistic two-configuration approximation.

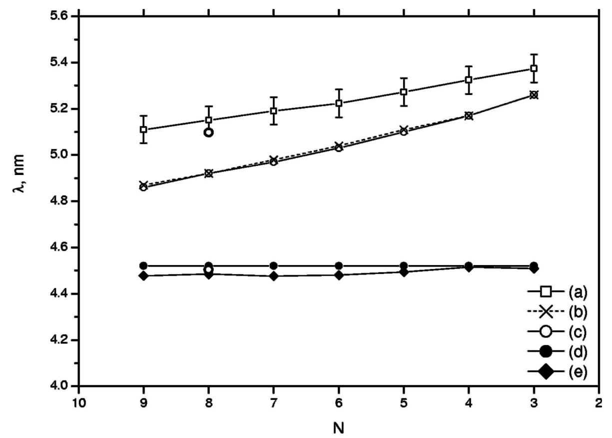

Fig. 3. Comparison of the average wavelengths of quasicontinuum band and satellite line in the experimental spectra of tungsten ions with the results of calculations. Quasicontinuum band: (a) experiment [13], (b) calculation using the collisional-radiative model [13], (c) calculations in the relativistic CI approximation (3). Satellite line: (d) experiment [13], (e) calculations in the relativistic CI approximation. The points near (b) and (d) curves for W^{30+} represent the results of an extended calculation with the additional ten configurations.

tungsten ions with an open $4d^N$ shell. Such a group of lines corresponds to the subarray of transitions (3) with one spectator 5s electron. These lines are also concentrated in a narrow interval due to the strong mixing of configurations $4p^54d^N5s$ and $4p^64d^{N-2}4f5s$.

The average wavelengths of quasicontinuum band and satellite line correspond fairly well to the values obtained in the EBIT experiment (Fig. 3). The position of the band calculated in the ground level approximation practically coincides with the result calculated in the collisional-radiative model [13]. In the present work we have also performed the more accurate calculations for one of the ions, W^{30+}, taking into account many additional configurations to the set (3) at $N = 8$, namely, $4p^54d^74f^2$, $4p^54d^74f5p$, $4p^64d^74f$, $4p^64d^54f^3$, $4p^64d^64f(5d{+}5g)$, $4p^44d^94f$ for the initial excited state and $4p^64d^64f^2$ for the ground state. The admixed configurations have been selected using the configuration mixing strength introduced in [18]. In Fig. 4 this spectrum is compared with the result of calculation using the set (3). The shape and width of the intense group of lines as well as the distribution of the satellite lines remain very similar to the result obtained for the smaller set of configurations. Some differences in the intensities of satellite lines appear because of using the average line width, instead of the line width determined for the separate lines, in the extended scale calculations. The average wavelengths of the quasicontinuum band and of the narrow group of satellite lines at 4.5 nm are shifted to larger values and practically coincide with experimental data. Such data are absent yet for the other group of satellite lines at about 2.2 nm.

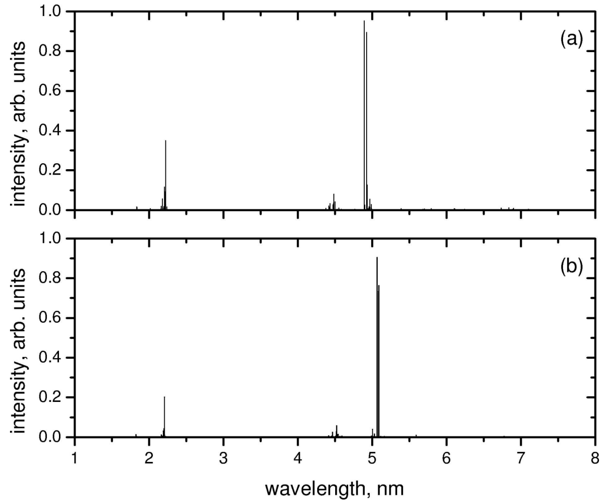

Fig. 4. Emission spectrum of W^{30+} obtained after the photoexcitation from the ground level. Results of the relativistic calculations: (a) in CI approximation (3), (b) additionally including the ten configurations indicated in the text.

3. Conclusions

Theoretical investigation of the configuration mixing with a symmetric exchange of symmetry in two different cases of medium and high ionization degrees has shown that some regularities established for the spectra of tungsten manifest themselves also in the spectra of tin and antimony. The comparison of the emission spectra calculated in two-configuration approximation with the semiempirical spectrum of Sn^{12+} and theoretical spectrum of W^{30+}, obtained using a large set of configurations, show that the integral characteristics of the intense group of lines are mainly determined only by SEOS correlations. On increasing the ionization degree the width of energy level spectrum as well as the interval of emission or excitation spectra tend to increase. However, there are two important exceptions. In the isoelectronic sequences with the numbers of $4d$ electrons $N \geq 3$ the width of the intense group of lines decreases due to the splitting of a $4d^N$ shell into the subshells and the suppression of transitions to the closed $4d^N_{3/2}$ subshell. On the other hand, when the coupling within a $4d^N$ shell is close to LS, the extremely narrow emission spectra excited from the ground level are obtained for the ions with the half-filled $4d^5$ electron shell.

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INTENSYVUMO SISTIPRĖJIMAS Sb, Sn IR W JONŲ EMISIJOS SPEKTRUOSE, ATSIRANDANTIS DĖL KONFIGŪRACIJŲ SU SIMETRIŠKU SIMETRIJOS PASIKEITIMU SUMAIŠYMO

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Santrauka

Nagrinėjamas intensyvių ir siaurų linijų grupių susidarymas dėl stipraus konfigūracijų sumaišymo jonų fotoabsorbcijos ir emisijos spektruose, atitinkančiuose šuolius $4p^5 4d^{N+1} + 4p^6 4d^{N-1} 4f \rightarrow 4p^6 4d^N$. Skaičiavimai reliatyvistiniu artutinumu atlikti Sn^{9+}–Sn^{12+} ir Sb^{10+}–Sb^{11+} jonams, kurie yra pagrindiniai kandidatai kuriant ultravioletinių spindulių šaltinį litografijai, ir volframo jonams W^{q+}, kurių intensyvi spinduliuotė sudaro nepageidaujamus nuostolius tokamako plazmoje. Parodyta, kad sumaišymas su kitomis sužadintomis konfigūracijomis turi mažai įtakos intensyviausių linijų grupės integrinėms charakteristikoms. Ypač stiprus spektro susiaurėjimas pasireiškia volframo jonams, kurių konfigūracijose yra daugiau kaip trys $4d$ elektronai, taip pat alavo ir stibio jonams su pusiau užpildytu $4d$ elektronų sluoksniu.