Functional Materials 13, No.1 (2006)

$M\alpha$ X-ray emission spectrum of multi-ionized Au atoms

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A model of $M\alpha$ X-ray emission has been proposed taking into account the main vacancy generation and migration channels within the M shell. Equation have been derived allowing the relative intensity calculation of Mα satellites ($S\alpha$). For Au, the $S\alpha$ values under the $M\alpha$ spectrum excitation by polychromatic emission of BCV-12 X-ray tubes with Cr and Cu anodes have been studied in experiment. The experimental $S\alpha$ values coincide (within the error limits) with the calculated ones. The model proposed has been concluded to describe correctly the Mα emission in elements having Z>70.

Предложена модель рентгеновской $M\alpha$-эмиссии, учитывающая основные каналы генерации и миграции вакансий внутри M-оболочки. Получены уравнения, позволяющие рассчитать относительные интенсивности $M\alpha$-сателлитов ($S\alpha$). Для элемента Au проведено экспериментальное исследование величины $S\alpha$ при возбуждении $M\alpha$-спектра полихроматическим излучением рентгеновских трубок БХВ-12 с Cr и Cu анодами. Экспериментальные и рассчитанные значения величины $S\alpha$ в пределах погрешности практически совпадают. Сделан вывод о том, что предложенная модель корректна для описания $M\alpha$-эмиссии в элементах $Z > 70$.

Thin films of noble metals, in particular, Au, are used widely in modern micro-electronic devices. Of a particular importance in those cases is the control of the film physical state that is defined to a great extent by the state of the structure electron subsystem. Among the diagnostic methods of the metal film electron subsystems, the X-ray emission spectroscopy of K and L bands are worth to be noted. Those methods made it possible to obtain data on the electron state density, in particular, near the Fermi level [1–3]. However, the $M\alpha$ X-ray spectroscopy was not used to study the thin films of heavy metals. Thus, it is of interest to develop a model of that emission and to use it for the film control.

When modeling the $M\alpha$ emission, it is to note that direct ionization of the M_i subshell ($i = 1-5$) of an atom by incident particles can be accompanied by radiative decay of the created vacancy with emission of a corresponding X-ray line of a M series, for example, $M\alpha$ line (M_5 to $N_{6,7}$ transition). However, in the case, when energy of such a particle is sufficient to ionize more inner M_i subshells, an M_i vacancy ($i \neq 1$) may be formed also due to the double ionization connected with the Coster-Kronig (CK) transitions, such as $M_i{-}M_jN$ and $M_i{-}M_jX$ (X = O, P). The contributions of such processes to the total generation cross section of M_i vacancy are rather significant [1, 2]. As a result of CK transitions and their cascades, the states arise with one or several additional vacancies in N, O or P shells. The radiative decay of M_i vacancy in the presence of N, O or P vacancies results in radiation of satellite lines which together with a corresponding X-ray emission line form a total spectral $M\alpha$ contour [3–6]. It is important to note that for $M\alpha$ lines radiated by atoms of heavy elements ($Z > 70$), the groups of $M_5N{-}N_{6,7}N$ transitions (M_5N satellites) differ by 5 to 9 eV from the corresponding $M\alpha$ line, whereas for $M_5X{-}N_{6,7}X$ transitions (M_5X satellites), such shifts do not exceed 1 or 2 eV [3]. Thus, the corresponding M_5N satellites for these elements, unlike the M_5X satellites, can be in principle singled out the total $M\alpha$ contour.

A number of works is known where the integral intensities of $M\alpha$-, $M\beta$- and $M\gamma$-lines of heavy elements were experimentally measured under various conditions of excitation. For example, at photoabsorption (investigated elements $70 \le Z \le 92$) [3], bombardment with α-particles (Hf to Th) [4], proton impact (Hg) [5], bombardment with F^{8+}, Li^{3+}, C^{5+}, H^+ ions (Au) [6]. The obtained intensity values were compared as a rule to calculation results of $M\alpha$-, $M\beta$- and $M\gamma$ X-ray production cross sections in which M_i–M_jN and M_i–M_jX CK transitions and cascades thereof were taken into account. However, the separation of M_5N-satellites from the total $M\alpha$ contour in [3–6] was not performed. The intensities of such satellite groups were not calculated separately. At the same time, use the relative intensities of the separated short-wave satellites expands number of the equations, which describe the intensity of M X-ray emission, giving more information of such description. For example, in the case of L series, the account of the relative intensities of L_3M_5-satellites of a $L\alpha_{1,2}$-line has allowed us in recent papers [7, 8] to determine a partial width of L_1 level connected with L_1–L_3M_5 CK transitions in atoms of W to Pt elements. In this paper, a model of $M\alpha$ X-ray emission which takes into account the most important generation and migration channels of vacancies in M_i subshells is proposed and applied to relative intensity determination of the M_5N satellites to the $M\alpha$ line. The relative intensity of M_5N-satellites are experimentally determined for Au excited by $K\alpha$ emission of Cr and Cu and the data obtained are compared to calculated results within the frame of suggested model.

Let us consider a separate type of $M\alpha$ satellites which represent radiative M_5–$N_{6,7}$ transitions in the presence of one additional vacancy in $N_{6,7}$ subshells. Let all possible processes be considered which may result in emission of $M_5N_{6,7}$ satellites. From here on, the following designations will be used: P_i^N, the probability of a process in which the appearance of a vacancy in i-th subshell ($i = M_1$ to M_5) is accompanied by ejection of one $N_{6,7}$ electron due to shake-off (SO) process; f_{ijN}, the yield of a CK transition of the M_i–$M_jN_{6,7}$ type where a vacancy is transferred from M_i to M_j subshell ($j > i$) and one of the $N_{6,7}$ electrons leaves the atom; ω_{MiMj}, the fluorescence yield for a radiative M_i–M_j transition; σ_i, the photoionization cross section of the M_i subshell; Γ_α, the partial width of M_5 level corresponding to the radiative M_5–$N_{6,7}$ transition; Γ_i, total width of the M_i level. We shall be restricted to the account for maximum two consecutive transitions within one shell and for one transition between shells. Thus, there are the following possible processes which result in arising of initial $M_5N_{6,7}$ states:

1) A vacancy arises in M_5 subshell and an $N_{6,7}$ SO process occurs. The process probability is:

$$K_1 = P^N_{M5}. \qquad (1)$$

2) A vacancy arises in M_4 subshell and transfers to M_5 one due to CK transition of the M_4–$M_5N_{6,7}$ type. The probability is:

$$K_2 = f_{45N}. \qquad (2)$$

3) A vacancy arises in M_3 subshell and transfers to M_5 one due to the following processes:

a) CK transition of the M_3–$M_5N_{6,7}$ type; b) $N_{6,7}$ SO process followed by radiative M_3–M_5 transition. The probabilities of those processes are:

$$K_3 = f_{35N} + P^N_{M3}\omega_{M3M5}. \qquad (3)$$

4) A vacancy arises in M_2 subshell and transfers to M_5 one due to the following processes:

a) CK transition of the M_2–$M_5N_{6,7}$ type; b) $N_{6,7}$ SO process followed by radiative M_2–M_5 transition; c) CK transition of the M_2–$M_3N_{6,7}$ type followed by radiative M_3–M_5 transition; d) radiative M_2–M_4 transition followed by CK transition of the M_4–$M_5N_{6,7}$ type. The probabilities of those processes are:

$$K_4 = f_{25N} + P^N_{M2}\omega_{M2M5} + f_{23N}\omega_{M3M5} + \omega_{M2M4}f_{45N}. \qquad (4)$$

5) A vacancy arises in M_1 subshell and transfers to M_5 one due to all possible SO, CK and radiative transitions. The probabilities of these processes are:

$$K_5 = f_{15N} + P^N_{M1}(\omega_{M1M5} + \omega_{M1M3}\omega_{M3M5}) + f_{12N}\omega_{M2M5} + f_{13N}\omega_{M3M5} + \omega_{M1M3}f_{35N} + \omega_{M1M4}f_{45N}. \qquad (5)$$

Summing up all the above, the intensity of a $M\alpha$ satellite in the case of additional vacancy in $N_{6,7}$ subshells can be written as:

$$I(M_5N_{6,7}) = (\sigma_5K_1 + \sigma_4K_2 + \sigma_3K_3 + \sigma_2K_4 + \sigma_1K_5)\frac{\Gamma_\alpha}{\Gamma_{M5} + \Gamma_{N6,7}}. \quad (6)$$

Basing on similar considerations, it is possible to derive equations for intensity calculation of M_5N_5-, M_5N_4-, M_5N_3-, M_5N_2- and M_5N_1-satellite groups. Then total intensity of $M\alpha$ satellites (I($M\alpha_{sat}$)) is determined as the sum of intensities of all satellite groups:

$$I(M\alpha_{sat}) = \sum_{k=1}^{7} I(M_5N_k). \quad (7)$$

It is important to note that in the present model, we neglect the satellites associated to radiative transitions in $M_5N_iN_i$ and M_5N_iX ionized atoms. The intensities of these satellites contribute to the total intensity of $M\alpha$ satellites no more than 1 %.

The intensity of the total $M\alpha$ contour was determined using equation presented in [9]. The $M\alpha$ line intensity ($I(M\alpha)$) was determined as a difference between the total contour intensity and that of the satellites. To calculate the relative intensity of $M\alpha$ satellites ($S\alpha = I(M\alpha_{sat})/(I(M\alpha))$ and to study those in experiment, thin gold films were used. This element was chosen because the fluorescence yield for Au is already significant enough and a satisfactory angular dispersion of the $M\alpha$ spectrum is realized. To calculate $S\alpha$, the following literature data were used: photoionization cross sections of M_i subshells [10], radiative transition rates for M_i subshells [11, 12], total and partial widths of M_i levels, yields of CK transitions and probabilities of SO processes [13–16]. The corrections for absorption of $K\alpha$ radiation and self-absorption of the $M\alpha$-line in thin Au films were taken into account.

The secondary $M\alpha$ spectra of Au were measured using a DRS-2 X-ray spectrograph in the first order of reflection from (10$\bar{1}$1) planes of a quartz single crystal. The spectra were excited by polychromatic radiation from BHV-12 X-ray tubes with Cr and Cu anods. The water-cooled X-ray tubes were operated at U = 30 kV and I = 60 mA. The fraction of secondary $M\alpha$ spectrum photons generated in these conditions due to bremsstrahlung in relation to the fraction excited by characteristic $K\alpha$ radiation of Cr and Cu does not exceed 3 %. So, the $M\alpha$ spectrum of Au can be believed to be excited by characteristic $K\alpha$ radiation of Cr and Cu only. The secondary X-ray emission spectrum of $M\alpha$ line of Au with $M\alpha$ satellites, excited by characteristic $K\alpha$ radiation of Cr is shown in Fig. 1. In the inset, the residual spectrum of $M\alpha$ satellites is shown. Experimental values of intensities of $M\alpha$ line and $M\alpha$ satellites were determined as the area under experimental contours thereof. The relative intensity of $M\alpha$ satellites were determined at an accuracy to within 10 %. The processing technique of experimental spectra is described in more details in [7].

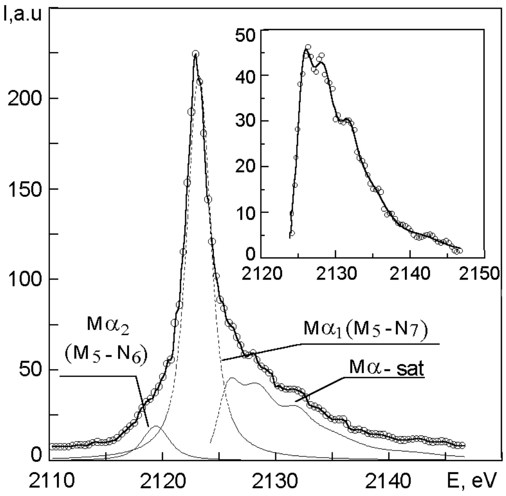

Fig. 1. The secondary X-ray emission spectrum of $M\alpha$-line of Au with $M\alpha$-satellites.

Data of calculations ($S\alpha$calc.) and experimental values ($S\alpha$exp.) are shown in Table, where $S(N_k) = I(M_5N_k)/I(M\alpha)$ denote rela-

Table 1. Theoretical and experimental values of relative intensities of $M\alpha$-satellites of Au excited by $K\alpha$-characteristic radiation of Cr and Cu.

	$S(N_1)$	$S(N_2)$	$S(N_3)$	$S(N_4)$	$S(N_5)$	$S(N_{6,7})$	$S\alpha$calc.	$S\alpha$exp.
Cr	0.002	0.005	0.013	0.019	0.031	0.471	0.541	0.522
Cu	0.002	0.005	0.015	0.021	0.035	0.523	0.601	0.571

tive intensities of M_5N_k satellite groups. It is seen that the calculated and experimental values coincide within the error limits. Thus, the suggested model describes correctly the process of $M\alpha$ emission. It is to note that the major contribution to the total intensity of $M\alpha$ satellites is caused by satellites connected with radiative transitions in $M_5N_{6,7}$ ionized atoms. Those are responsible for more than 85 % of the total intensity from all $M\alpha$ satellite groups.

To conclude, a model of X-ray $M\alpha$ emission which allows to determine the relative intensities of $M\alpha$ satellites is proposed in this work. This model also can be used to determine the contributions from different multiionized states. So, the model can be recommended for the description of X-ray $M\alpha$ emission in elements $Z > 70$.

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Рентгенівський емісійний $M\alpha$-спектр кратноіонізованих атомів Au

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Запропоновано модель рентгенівської $M\alpha$-емісії, яка враховує основні канали генерації та міграції вакансій у середині M-оболонки. Отримано рівняння, що дозволяють розрахувати відносні інтенсивності $M\alpha$-сателітів ($S\alpha$). Для елемента Au проведено експериментальне дослідження величини $S\alpha$ при збудженні $M\alpha$-спектра поліхроматичним випромінюванням рентгенівських трубок БХВ-12 з Cr та Cu анодами. Експериментальні та розраховані значення величини $S\alpha$ у межах похибки практично співпадають. Зроблено висновок про те, що запропонована модель коректна для опису $M\alpha$-емісії в елементах $Z > 70$.