

Mo L X-rays Relative Yield Ion Energy Dependence

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Abstract. In previous works, it was shown that the relative yields of W L x-rays emitted under proton irradiation depend on the ion beam energy and can be used to establish intensity ratio variation patterns (IRVP) [1], which may then be used to distinguish between different chemical species of the same element. In the present work, Mo L_{α} , $L_{\beta 3,4}$ and $L_{\beta 2,15}$ -spectra were obtained using the high resolution Johansson type crystal spectrometer at the Micro Analytical Center of the Josef Stefan Institute at Ljubljana, and Mo, $MgMoO_4$ and $(NH_4)_6Mo_7O_{24} \cdot 4(H_2O)$ L-spectra were obtained using a Si(Li) detector of ITN at Lisbon, for several proton beam energies between 0.4 and 1.5 MeV (corresponding to reduced velocities values between 0.7 and 1.4). Spectra deconvolution, whenever required, used a Bayesian Inference process to reduce errors due to spectra fitting. In the case of the Mo foil and the $MgMoO_4$ samples, ultra pure materials were used to avoid any possible target contamination. In the case of $(NH_4)_6Mo_7O_{24} \cdot 4(H_2O)$ this was not possible so P.A. material was used. In this communication observed $L_{\beta 2,15}/L_{\alpha 1}$ and $L_{\beta 2,15}/L_{\beta 3,4}$ ratio variability presented but unexplained in a previous work [2] will be discussed based on new evidence and comparison of data relative to different chemical species. Other Mo intensity ratio variation patterns are also presented and discussed.

Keywords: RYIED, Intensity Ratio Variation Patterns, PIXE, X-rays.

INTRODUCTION

PIXE analysis using K_{α} or L_{α} transitions is presently a common task. Nevertheless, the use of other x-ray lines still remains significantly unexplored, although it is presently well known that information on the electronic environment of the radiating ion is present therein [3-7]. Furthermore, a proper accounting for the intensity of these other lines may be essential to achieve a correct quantification of all elements present in a sample. Several reasons can justify discrepancies between experimental and theoretical values. An example can be found (among many others) in the work of Acharya [8], which by studying various Mo compounds determined an abnormal value for the $K_{\alpha 2}/K_{\alpha 1}$ intensity ratio that he attributed to multi-ionization, shake-off and Coster Kronig processes. In the present work results are presented for $L_{\beta 2,15}/L_{\beta 3,4}$, $L_{\gamma 2,3}/L_{\beta 3,4}$, $L_{\gamma 1}/L_{\beta 1}$ and $L_{\beta 2,15}/L_{\alpha 1}$, the first being used for comparison to high resolution data while the last three correspond to identical sub-shell transitions for L1, L2 and L3 sub-shell respectively (see table1). A comparison of data relative to different chemical species is discussed.

MATERIAL AND METHODS

In the present study three compounds of Mo were irradiated at ITN 2.5 MV Van de Graaff, namely Mo foil, $MgMoO_4$ and $(NH_4)_6Mo_7O_{24} \cdot 4(H_2O)$. The ITN PIXE setup used, described in detail elsewhere [9], makes use of a Si(Li) 150 eV resolution detector kept at an angle of 110° relative to the beam direction. In the case of this experiment, a Ta collimator having a thickness of 1mm and a diameter of 0.7mm was used in front of the Si(Li) detector. Spectra were collected for proton beams having energies 0.35, 0.58, 1.00 and 1.52 MeV (after crossing a $0.8\mu m$ thick Al diffuser foil). A spectrum having roughly 2×10^6 counts on the Mo- L_{α} was acquired for each ion beam energy value. An identical Mo foil sample was also irradiated at the Micro Analytical Center (MIC) of the J. Stefan Institute, Ljubljana. where proton beam energies of 0.3, 0.4, 0.6, 0.8, 1.0, 1.5 and 2.0 MeV and beam currents of $1\mu A$ were used. The proton beam incidence angle and the X-ray emission angle relative to the target surface were of 45° . Johanson type curved crystal spectrometer was used, the detailed description

of which can be found in ref. [10]. Experimental conditions were adjusted in the order to optimize sampling time and counting statistics (e.g.: 2000 counts at 0.3 MeV and 40000 at 2.0 MeV in the $L_{\alpha 1}$ line). As the full range of the spectrometer for a single measurement covers not much more than 70 eV, the spectra beam energy dependence was studied for $L_{\alpha 1}$, $L_{\alpha 2}$ and for $L_{\beta 2,15}$, $L_{\beta 4}$ and $L_{\beta 3}$. The $L_{\beta 4}/L_{\beta 3}$ intensity ratio was discussed in a previous work.

Spectra fitting was carried out using the core of the new DT2 code, present in another communication at this conference [13], and these making use of a Bayesian inference routine for determination of the errors.

RESULTS AND DISCUSSION

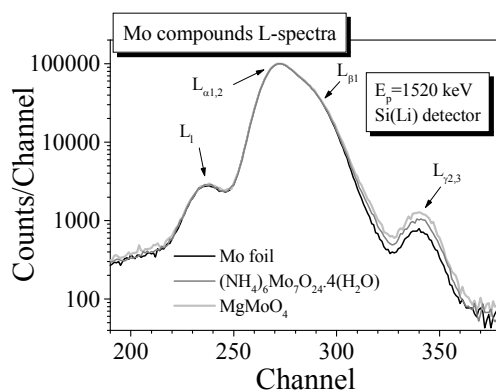


FIGURE 1. Superposition of L x-ray energy region spectra of Mo compounds irradiated with proton beam of 1520 keV and collected using a Si(Li) detector. Spectra are normalized to the $L_{\alpha 1}$ of Mo foil. Spectra were collected at ITN.

In Fig. 1 spectra of Mo foil, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24.4}(\text{H}_2\text{O})$ and MoMgO_4 compounds irradiated using a 1.52 MeV proton beam are shown. Spectra are normalized to the $L_{\alpha 1}$ of Mo foil. At first, differences in the three spectra clear for the $L_{\gamma 2,3}$ x-ray line, may be due strictly to auto-absorption differences.

In table 1 the energy of the Mo L x-rays lines used in the fitting process are presented in, Siegbahn and IUPAC notation as well as in atomic orbital transition description. In order to reduce the errors the $L_{\beta 3}$ and $L_{\beta 4}$ lines were fitted as a single line due to its proximity in the spectra (less than 18eV), see table 1.

This experiments with Mo L x-rays was made taking care to collect high counting statistics spectra in order to reduce the errors and the fitting.

In Figure 2, the $L_{\beta 2,15}/L_{\beta 3,4}$ experimental intensity ratios are shown for: Mo foil sample collected using the high resolution detector, and for three compounds of Mo: Mo foil, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24.4}(\text{H}_2\text{O})$ and MoMgO_4 , collected with a Si(Li) detector as function of the incident proton beam energy. It is interesting to realize that the intensity ratio has the same curve type for all four cases. Considering the errors bars of the intensity ratios obtained for Mo compounds collected with Si(Li), we can fit two guiding lines to these intensity ratios. From the results from Mo foil collected using high resolution, and also using two guiding lines, it can be seen that at a value of 900 keV for ion beam energy there is a change in behavior of the ratio, from almost constant for energies larger than 900 keV to a factor of two times more for beam energies values lowers than 900keV. The fact that there are only three points defining this response for Mo thick sample collected using the high resolution detector does not render the result weaker as in this case there is no reason for numerical or any other type of problem, to be present in the fitting of the peaks.

TABLE 1. L x-ray lines of Mo. X-ray lines are described using the Siegbahn notation, but also the IUPAC notation and the electron wave function transition [12]. The corresponding energy, according to Deslattes [14], are also presented.

Siegbahn	IUPAC	Wave functions	Energy (keV)
$L_{\beta 4}$	L_1M_2	$3p_{1/2} \rightarrow 2s_{1/2}$	2.45568
$L_{\beta 3}$	L_1M_3	$3p_{3/2} \rightarrow 2s_{1/2}$	2.47307
$L_{\gamma 2,3}$	$L_1N_{2,3}$	$4p_{1/2,3/2} \rightarrow 2s_{1/2}$	2.83065
L_1 edge			2.8806
$L_{\beta 1}$	L_2M_4	$3d_{3/2} \rightarrow 2p_{1/2}$	2.39483
L_{η}	L_2M_1	$3s_{1/2} \rightarrow 2p_{1/2}$	2.12026
$L_{\gamma 5}$	L_2N_1	$4s_{1/2} \rightarrow 2p_{1/2}$	2.56326
$L_{\gamma 1}$	L_2N_4	$4d_{3/2} \rightarrow 2p_{1/2}$	2.62352
L_2 edge			2.62730
$L_{\alpha 1}$	L_3M_5	$3d_{5/2} \rightarrow 2p_{3/2}$	2.29319
L_1	L_3M_1	$3s_{1/2} \rightarrow 2p_{3/2}$	2.01571
$L_{\alpha 2}$	L_3M_4	$3d_{3/2} \rightarrow 2p_{3/2}$	2.28988
$L_{\beta 6}$	L_3N_1	$4s_{1/2} \rightarrow 2p_{3/2}$	2.45568
$L_{\beta 2,15}$	$L_3N_{4,5}$	$4d_{3/2,5/2} \rightarrow 2p_{3/2}$	2.51833
L_3 edge			2.52356

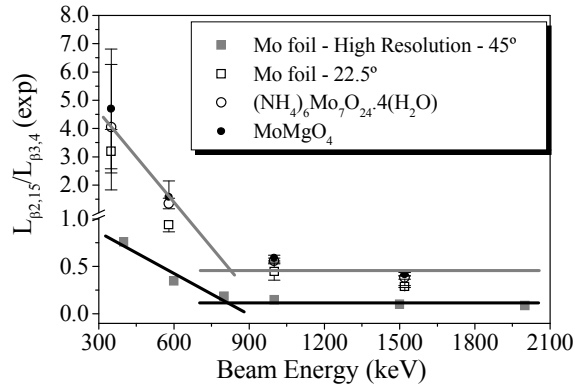


FIGURE 2. $L_{\beta 2,15}/L_{\beta 3,4}$ ratios as a function of the ion beam energy for a 99.995% pure Mo 1mm thick foil, as measured at the high resolution Johanson type curved Crystal spectrometer of the JSI. This ratio is also presented for: 99.995% pure Mo 1mm thick foil, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4(\text{H}_2\text{O})$ and MoMgO_4 thick samples collected with Si(Li) detector at ITN. The two lines in black and in gray are guiding lines.

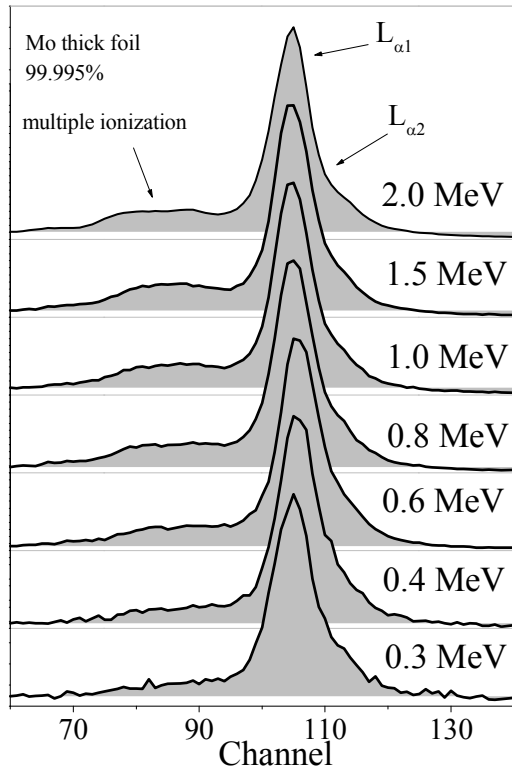


FIGURE 3. Superposition of the evolution of $L_{\alpha 1,2}$ energy region spectra for a pure Mo target bombarded using a proton beam with energies between 0.3 to 2.0 MeV at the high resolution Johanson type curved crystal spectrometer of the Josef Stefan Institute, Ljubljana. The change in shape of the multiple ionization region is clear.

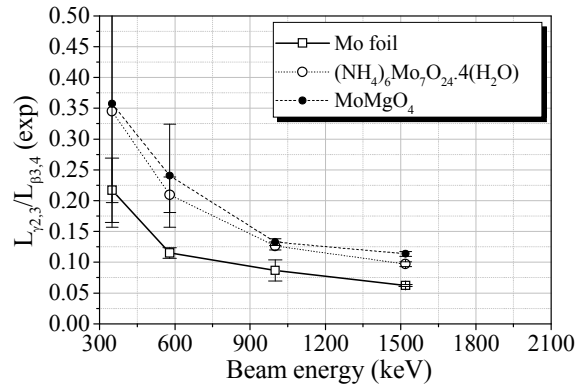
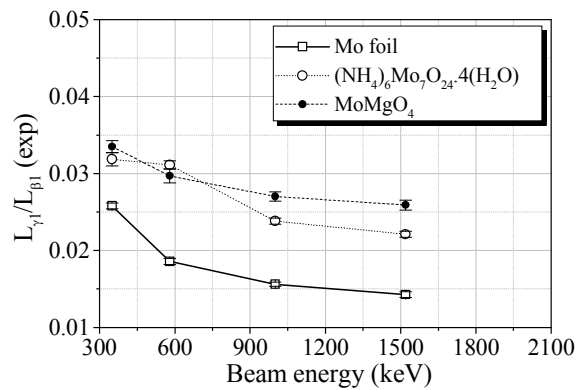
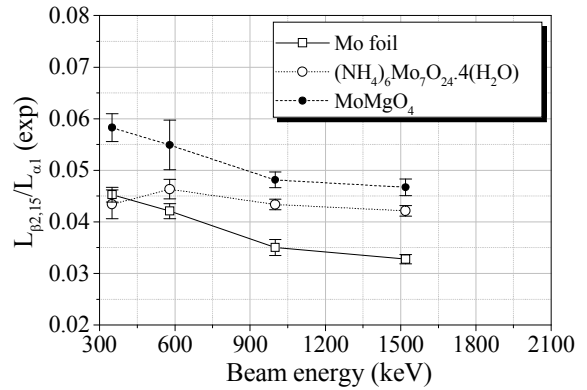


FIGURE 4. $L_{\beta 2,15}/L_{\alpha 1}$, $L_{\gamma 1}/L_{\beta 1}$, $L_{\gamma 2,3}/L_{\beta 3,4}$ intensity ratios, corresponding to L1, L2 and L3 sub-shell, respectively. Spectra were collected at ITN with proton beams having energies 0.35, 0.58, 1.00 and 1.52 MeV.

When we compare this results with the results obtained from Si(Li) detector, we see that the tendency of the guiding lines are the same, which shows that the point where an alteration exist in the intensity ratio appears to be the same. This is a good indication that the fitting process used for the spectra collected using the Si(Li) detector reproduces the results obtained with high resolution where there is no reason for numerical or any other type of problem, to be present in the

fitting of the peaks. The curve of intensity ratio obtained for Mo foil appearing lower for the experiment made at the J. Stefan Institute than the curve obtained with Si(Li) detector, merely reflects the differences in the incident angle used in both cases (45° for high resolution and 22.5° for Si(Li) detector).

In figure 3, we present $L_{\alpha 1,2}$ spectra collected for different incident ion beam energies at the high resolution Johanson spectrometer. Note that $L_{\alpha 1}$ and $L_{\alpha 2}$, still appear like a single line once the difference in energy is less than 4 eV (table 1).

It can be readily seen that a multiple ionization structure grows up with the increase of ion beam energy. This contribution of multiple-ionization appears like constant above an ion beam energy 1000 keV.

In figure 4, the intensity ratios, $L_{\beta 2,15}/L_{\alpha 1}$, $L_{\gamma 1}/L_{\beta 1}$, $L_{\gamma 2,3}/L_{\beta 3,4}$, corresponding to L3, L2 and L1 sub-shell transitions, respectively, are present for the three Mo compounds using ion beam energies between 0.35 and 1.52 MeV. The intensity ratios are calculated to the most intense line in the corresponding L sub-shell, namely, $L_{\beta 3,4}$, $L_{\beta 1}$ and $L_{\alpha 1}$. The dependence of intensity ratios with incident ion beam energy, already observed in the L1-shell [2], were also observed for L2 and L3 shell. In all the intensity ratios, the values of the ratio decrease with the increasing of the ion beam energy, as would be expected from the variation of autoabsorption.

Relatively to transitions for L3 and L2 sub-shells, $L_{\beta 2,15}/L_{\alpha 1}$ and $L_{\gamma 1}/L_{\beta 1}$ intensity ratios, the curve for the three compounds are different for all cases.

Relatively to the $L_{\gamma 2,3}/L_{\beta 3,4}$ intensity ratio, transitions for L1 sub-shell, the intensity ratios are very similar for $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4(\text{H}_2\text{O})$ and MoMgO_4 , but highest when compared with Mo foil.

CONCLUSIONS

It was shown that the intensity ratio $L_{\beta 2,15}/L_{\beta 3,4}$, obtained using high resolution and the Si(Li) detector for a pure Mo 1 mm thick foil lead to the same curve type. Furthermore, this intensity ratio presents a point, where there is a change in behavior of the ratio, already seen in previous work.

The $L_{\alpha 1,2}$ spectra collected using high resolution shows that the multiple ionization structure grows with the increase of ion beam energy up to an energy identical to the crossing slopes energy for the line ratios variations. Above this ion beam energy the multiple ionization structure remains essentially constant. We are thus led to conclude that multiconfiguration effects are behind this course effect reported here and also in previous works [1,2].

ACKNOWLEDGMENTS

This work was partially supported by the Portuguese Foundation for Science and Technology, FCT, through a PhD fellowship with the following reference SFRH/BD/27557/2006.

This work is also funded in the framework of project REEQ/377/FIS/2005 of the Portuguese Foundation for Science and Technology, FCT.

REFERENCES

- 1 M. A. Reis, P. C. Chaves, J. C. Soares, Nuclear Instruments and Methods in Physics Research B 229 (2005) 413-424.
- 2 P. C. Chaves, M.A. Reis, N. P. Barradas, Matjaž Kavčič, Nuclear Instruments and Methods in Physics Research B (In press)
- 3 S. Raj, H. C. Padhi, D. K. Basa, M. Polasik, F. Pawłowski; Nucl. Instr. And Meth. B 152 (1999) 417-424.
- 4 S. Raj, H. C. Padhi, M. Polasik; Nucl. Instr. And Meth. B 160 (2000) 443-448.
- 5 I. Török, T. Papp, J. Pálkás, M. Budnar, A. Mühleisen, J. Kawai, J.L. Campbell, Nucl. Inst. and Meth. Phys. Res. B 114 (1996) 9-14
- 6 F. Pawłowski, m. Polasik, S. Raj, H.C. Padhi, D. K. Basa, Nucl. Instr. and Meth. in Phys. res. B 195 (2002) 367-373
- 7 V. P. Petukhov, I. Torok, M. Terasawa; Nucl. Instr. And Meth. B 109/110 (1996) 105-108.
- 8 B. S. Acharya and R. Sakthivel, X-Ray Spectrometry, Vol.23, 236-241 (1994).
- 9 M. A. Reis, P. C. Chaves, V. Corregidor, N. P. Barradas, E. Alves, F. Dimroth, A. W. Bett, X-Ray Spectrom. 34 (2005) 372-375.
- 10 Matjaž Kavčič, A.G. Karydas, Ch. Zarkadas, Nuclear Instruments and Methods in Physics Research B 222 (2004) 601-608.
- 11 L. C. Alves, A. P. Jesus, M. A. Reis, Nuclear Instruments and Methods in Physics Research, B109/110 (1996) 129-133.
- 12 R. Jenkins, R. Manne, R. Robin and C. Senemaud, Pure and Applied Chemistry, **63** (1991) 735-746.
- 13 M.A. Reis, P.C. Chaves, C. Pascual-Izarra, L.C. Alves, N. P. Barradas, this conference, PII-1.
- 14 Richard D. Deslattes, Ernest G. Kessler, P. Indelicato, L. De Billy, E. Lindroth, J. Anton, Reviews of Modern Physics, volume 75, January 2003.