Comparative study on non-linear and linear least square analyses applied to X-ray induced Auger electron spectroscopy transitions

Anna Gagliardi,[1] N. Fairley,[2] S. Béchu[1]

[1] Institut Lavoisier de Versailles (ILV), Université de Versailles Saint-Quentin-en-Yvelines, Université Paris-Saclay, CNRS, UMR 8180, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France.

[2] Casa Software Ltd, Bay House, 5 Grosvenor Terrace, Teignmouth, Devon TQ14 8NE, United Kingdom.

With the exception of the modified Auger parameter, X-ray induced Auger electron (X-AES) transitions aren't exploited to their full potential. Indeed, they can provide as much information (oxidation degree, chemical environment, atomic composition) as the classic photopeaks used in XPS, but their shapes' complexities limit their decompositions.

We offer here to explore the decomposition of Ga $L_3M_{4,5}M_{4,5}$ and In $M_{4,5}N_{4,5}N_{4,5}$ X-AES lines by comparing two approaches: the non-linear [1] and the linear [2] least square analyses. By combining non-linear and linear fitting procedures, PCA, and vectorial method [3], those two analyses have been implemented on the materials $Cu(In_xGa_{1-x})Se_2$ and InSb, to unveil their surface oxidation when exposed to different atmospheres. The growth of oxide phases (Ga_2O_3 and In_2O_3, determined by PCA, vectorial method and by comparison with reference spectra) was monitored on the X-AES lines with non-linear and linear approaches, showing a very good coherence between both, as illustrated in Fig 1 for the In $M_{4,5}N_{4,5}N_{4,5}$ X-AES transition of InSb. We will provide keys to perform non-linear and linear least squares analysis on X-AES lines, to explore new approaches for chemical determination.

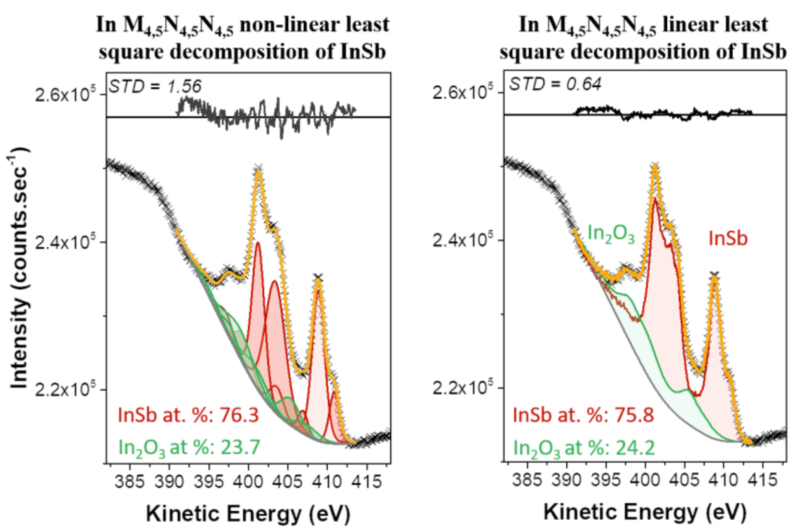

Figure 1 Curves to fitted data of InSb using non-linear (left) and linear (right) approaches.

[1] J.J. Moré, Numer. Anal. **630**, 105 (1978).
[2]G.H. Golub and C. Reinsch, Linear Algebr. **420**, 403 (1971).
[3] S. Béchu et al., Appl. Surf. Sci. **447**, 528 (2018).

+ Author for correspondence: solene.bechu@uvsq.fr

Supplementary Pages (Optional)

In Figure S1, we provide the example of Ga $L_3M_{4,5}M_{4,5}$ non-linear and linear least square approaches for CIGS material after aging. When using the non-linear approach, 5 arbitrary photopeaks are necessary to simulate the CIGS environment and 5 others for the Ga_2O_3 one. The fit results thus in a decomposition with 10 photopeaks while reference spectra of Ga in CIGS and in Ga_2O_3 are injected within the linear least square decomposition. If the fit is easier to perform with the linear least square decomposition (less error), its quality is slightly improved when using the non-linear least square decomposition approach. This aspect will be also evocated.

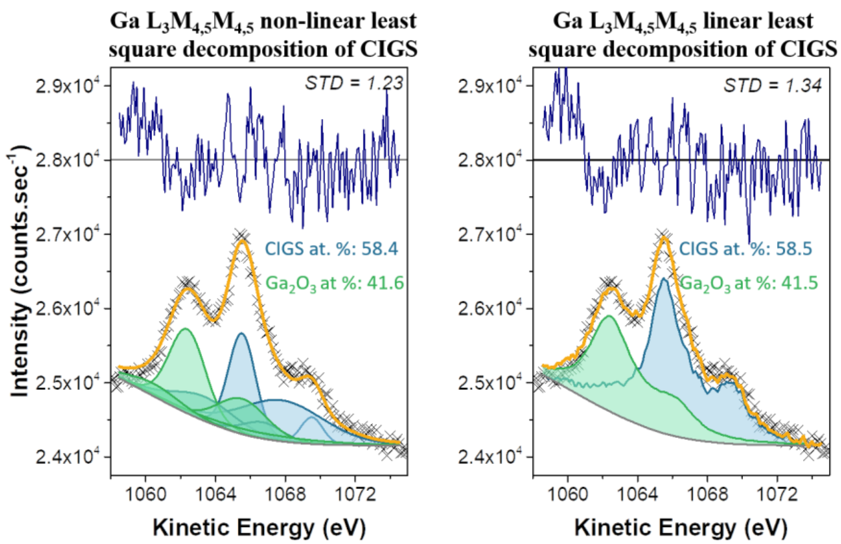

Figure S2 Curves to fitted data of CIGS using non-linear (left) and linear (right) approaches.

To show the coherence of the two approaches over a set of evolving data, we followed the percentage of Ga_2O_3 growth in CIGS Ga $L_3M_{4,5}M_{4,5}$ X-AES transition over time. Table S1 resumes this evolution for the non-linear and the linear approaches and the relative errors remain inferior to 5% for all the comparative data.

		t_0	t_1	t_2	t_3	t_4	t_5	t_6	t_7	t_8
Ga_2O_3 at. %	Non-linear approach	0.1	27.9	35.2	39.6	42.9	41.3	45.4	46.3	53.4
	Linear approach	0.0	27.6	34.3	39.1	42.3	41.1	45.9	45.9	53.1
Relative error (%)		0.0	1.1	2.6	1.3	1.4	0.5	1.1	0.9	0.6