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Title: Hard X -Ray Photoelectron Spectroscopy (HAXPES) characterisation of electrochemical passivation oxide layers on Al-Cr-Fe Complex Metallic Alloys (CMA)

Article Type: Short Communication

Keywords: Electrochemical passivation, Hard X-Ray Photoelectron Spectroscopy (HAXPES), Al alloys, Complex Metallic Alloys, composition depth profiling, oxide/hydroxide.

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Abstract: A Hard X-Ray Photoelectron Spectroscopy (HAXPES) characterisation of the passivation layers formed by electrochemical polarisation of corrosion resistant Al-Cr-Fe complex metallic alloys (CMAs) is presented. Employing a large range of X-ray excitation energies from 2.3 to 10.0 keV allowed identifying (by cross-correlating results of different excitation energies) and resolving the depth distributions of Al- and Cr- oxide and hydroxide species in the (Al,Cr)-passive layer through the whole film thickness, down to the oxide- alloy interface. Simultaneous analyses of the shallow Al 2s and deep Al 1s core level lines (which are more bulk- and surface-sensitive, respectively) provided complementary information to effectively resolve the relative contributions of hydroxide and oxide species as a function of depth below the surface. The Cr threshold concentration necessary to obtain passive film stabilisation at pH 1 was found to be 18 (at %).

*a.Cover Letter

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Reference: revised manuscript EC14-283

Dear Prof Compton

We are grateful for the useful comments of the Referees.

All points raised by the Referees have now been dealt with in the revised version of the manuscript (see enclosed our response to Referee's comments, with corresponding changes in the revised manuscript marked yellow).

We hope that the revised manuscript can now be accepted for publication in Electrochemistry Communications.

Zürich, 10th April 2014

Best Regards,
Alessandra Beni and collaborators

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***b. Response to Reviewers**

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Response to Reviewer 1

a) This is an interesting and generally competently presented paper. However it is not so original or innovative as the authors seem to believe. Hard XPS has been established over the past dozen years or so as a technique which probes deeper into the bulk than conventional XPS due to the increase in the electron pathlength and this paper is simply an application of this very well established principle to a specific technological problem.
So the first mandatory change is to remove all the hyperbole - starting with the word "new" as the second word in the abstract and in the research highlights and progressing for example through to "Quite remarkably" on line 152.

We acknowledge the criticism of the Reviewer. As requested, we removed all hyperbole statements in the revised paper. We fully agree that HAXPES is a well-established technique by now. Nevertheless, we would like to point out that the full potential of HAXPES has been rarely used to tackle problems related to the depth-resolved chemical constitution of relatively thick (as compared to the inelastic mean free path) passive oxide layers (6-7nm), as formed by electrochemical anodic polarisation. This is also evidenced from the limited number of HAXPES studies reported in the fields of electrochemistry and corrosion science. The present paper especially demonstrates the advantage of HAXPES when using energy dependent analysis and correlation for studying oxide/hydroxide distributions in thick passive oxide layers. This is the reason why we decided to submit this work specifically to Electrochemistry Communications and not a surface science journal.

b) The paper appears limited in that even though dealing with an Al-Cr-Fe alloy no data for Fe core lines are presented. Such data should be added if available or it should be explained why Fe is ignored.

We acknowledge the criticism of the Reviewer and apologise for omitting a discussion of the Fe core level lines. The Fe $2p_{3/2}$ core-level lines were obviously also measured and evidenced that Fe from the alloy is not incorporated in the grown oxide layers (i.e. only a small metallic Fe component is detected). In accordance with the Reviewers comment, we now included a corresponding comment in the revised letter: see lines 117-119.

c) The analysis of the Al 1s core line appears incorrect. It is not credible that there should be +1.6 eV and +2.7 eV shifts in the Al 2s core region between Al metal and its oxide and hydroxide, but no shift in the Al 1s region between oxide and hydroxide even though the oxide/hwith hydroxide peak is shifted by +2.5 eV from Al metal. The problem seems two fold. Firstly the Al 1s level obviously suffers more pronounced

lifetime broadening than the 2s level. This should be made clear to readers by redrawing figure 1 with Al 1s and Al 2s spectra presented over the same energy range and with the same scaling.

As recommended by the Reviewer, we have redrawn Fig. 1 with the Al 1s and Al 2s spectra presented over the same energy range and with the same scaling. Indeed, the updated figure much better visualises the different intrinsic widths of the Al 1s and Al 2s core level lines.

The curve fit to the Al 1s core line does not look convincing - an unexplained tail is taken up by a peak at around 1565 eV binding energy whose origin is not explained in the text. It looks to me the authors could do a better and physically plausible fit using components with about the same shifts as in the 2s region and without the mystery peak at 1565 eV.

Concerning the fitting of the measured Al 1s spectra, an additional figure of a reconstructed Al 1s spectrum pertaining to an *excitation energy of 10 keV* was added, which indeed indicates that the oxidic Al 1s envelope can also (i.e. as for the Al 2s spectrum) be fitted with an oxide and a hydroxide component at + 1.6 eV and + 2.5 eV, respectively (Fig. 1d). As recommended by the Reviewer, we have redone the fitting of the Al 1s spectra including these two components.

Strikingly, the Al 1s photoelectron line is much more surface sensitive and thus mainly probes the surface-adjacent hydroxylated region of the passive layer. Hence, the Al 1s main peak mainly constitutes the hydroxylated part of the oxide layer, whereas the oxidic Al 2s main peak contains significant contributions from both the (interface-adjacent) oxide and the (surface-adjacent) hydroxide regions. The corresponding discussion in the paper has been updated.

For the XPS assignment, please also have a look at Table A1 as reported below (Appendix of this response Letter).

d) Mystery 3rd peaks in the Al 2s and Cr 2p spectra excited at 2.3 keV should also be explained. Finally Cr 2p data excited at 6 keV should be added for completeness.

We acknowledge the criticism of the Reviewer. The assignment of the fitted Al , Cr and O peaks has been gathered in Table A1 of the response letter (Appendix of this response Letter). This minor component in the fitted Al 2p spectra is attributed to the presence of small amount of sulphates on the top surface (originating from the sulphuric acid in solution). This surface component is only very minor and therefore only detectable at low X-Ray energies (2.3keV).

Concerning the Cr 2p spectra at 6keV: unfortunately, the measurements for the Cr 2p core level line at 6 keV could not be recorded for the 27%Cr alloy (due to time constraints at the synchrotron). However, this missing information does not affect the interpretation of the results.

Response to Reviewer 2

This paper reports the hard XPS analysis of Al-Fe-Cr alloys. Specifically, the nature of the passivating layer is addressed. The measurement of the Al 1s peak is novel for this material system and also clearly advantageous, as it shows definite difference in oxide:hydroxide ratio compared with the Al 2s. This is correctly interpreted by the authors in terms of the surface sensitivity of the two peaks.
Also the angle resolved measurements of the Cr:Al ratio provide useful information on the depth distribution of these elements.

We thank the Reviewer for acknowledging the novelty and scientific quality of our work.

1. Overall, there is totally insufficient information given on the procedure used to peak fit the spectra. This is important as several of the conclusions depend on interpretations of the fitted model (e.g. oxide:hydroxide ratios). No information is given on model constraints used (eg FWHM, positions) or peak shapes applied (important for metal peaks and multiplet split peaks such as Cr3+ 2p). As several of the points below show, I believe there are some serious problems with the peak fitting or the conclusions drawn therefrom, and the lack of information about the procedure used makes it impossible to judge how meaningful the fittings are.

As requested by the Referee, we have added more details concerning the XPS fitting procedure (lines 103-108 and Appendix of the Response Letter). The lineshapes of the metallic peak components have been determined from the measured spectra of the clean alloy samples. Here it is noted that, due to the variation of the energy resolution with the excitation energies (different source/analyser resolution, use of post-monochromators), the lineshape parameters of the fitted metallic and oxidic components differ for each excitation energies. As an example, a Table with all fit parameters for an excitation energy of 2.3 keV is reported in the Appendix of the Response Letter (also giving corresponding reference data from the NIST database and the literature). Unfortunately, due to the strict length constraints for the letter version from the publisher, we cannot present the full details of the fitting procedures. All more specific technical aspects of the peak assignment and fitting procedure will be presented in more detail in a full paper on the same topic to be published at a later stage in a surface science related journal. The contribution on Electrochemistry Communications presented here especially focusses on the application of HAXPES for determination of the depth-resolved chemical constitution of electrochemically formed passive layers. We hope that the additional details on the fitting procedure, as provided in the revised version of the letter, is satisfactory.

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2. The authors' fitting of the Cr 2p peaks, and the conclusions they draw from them is especially problematic. On page 8, lines 150-152, the authors claim that the Cr oxide and hydroxide peaks are "unequivocally resolved by HAXPES". This is absolutely not the case. The peaks fitted as 'oxide' and 'hydroxide' (fig 2 b and e) are heavily overlapped and therefore the parameters of the fitted components will be highly correlated, preventing definitive determination of either the energy or intensity. It's conceivable that the authors meant in page 8 line 150-152 that the oxide and hydroxide peaks together were resolved from the metal peak. If so this is not remarkable and can be achieved with lab-based XPS for Cr 2p.

With our statement ‘unequivocally resolved by XPS’, we would like to emphasise that we could not only clearly identify a shoulder in the measured peak envelope, but also qualitatively establish the depth distribution of the oxide and hydroxide components by tracing the variation of the intensity ratio of the resolved oxide and hydroxide contributions as a function of the kinetic energy of the detected photoelectrons (which depends on the excitation energy and the specific core-level under study). At specific excitation energies, the respective Cr or Al core level spectra only contained one of the two components, which strongly supports our statement ‘unequivocally resolved by XPS’. Nonetheless, we acknowledge the comment of the reviewer and modified the corresponding statements in the revised letter (lines 131-133, 165-166).

3. It appears from Fig 2b, 2e that the authors have fitted the Cr3+ 2p peak with a symmetric component - it is well known that this peak, for example in Cr2O3, is highly asymmetric due to multiplet splitting. Not taking this into account will invalidate the analysis of the Cr oxide to hydroxide ratios.

We previously collected HAXPES data for a Cr_2O_3 single crystal at a different synchrotron beamline (with a lower spectral resolution), but did not find a pronounced asymmetry of the *oxidic* Cr 2p core-level line; i.e. it could be well-described with a symmetric lineshape. Even if there would be a considerable asymmetry of the Cr 2p peak and the oxide/hydroxide ratio indeed would be affected, our conclusions concerning the chemical constitution of the passive oxide layer would be equally valid, the way they are formulated in the letter.

4. The fitted Cr metal component in Fig 2b and 2e appear to be a different shape, which is not explained.

Here it is emphasised that, due to the variation of the energy resolution with the excitation energy (different source/analyser resolution, use of post-monochromators), the lineshape parameters of

the fitted metallic and oxidic components differ for each excitation energies. The lineshapes of the metallic peak components have been straightforwardly determined from the measured spectra of the clean alloy samples. The instrumental origin for the excitation-energy-dependent peak shapes has now been mentioned in the revised version of the letter.

5. In Fig 2b a component is fitted around 579.5 eV which is not identified in the text and appears to be absent in Fig 2e.

We acknowledge the criticism of the Reviewer. This minor component in the fitted fig. 2b spectra is attributed to small amount of sulphate bond to Cr on the surface as a result of the interaction with the electrolyte. This surface component is detectable at low X-Ray energies (2.3keV). The assignment of the fitted Al , Cr and O peaks has been gathered in Table A1 of the response letter (Appendix of the Response Letter).

6. Turning to the O1s peak fitting, again the authors overstate. On page 8, line 155-156 "the chemical shift of 1.2 eV between Al/Cr hydroxide (533 eV) and a Cr oxide (531 eV) bonding environment can be unambiguously resolved." This is certainly not true. Again the fitted O1s peaks shown in Fig 2 are heavily overlapped. There is nothing unambiguous about this fitting - the energy and intensity of the components cannot be known accurately. There are infinitely many models that would fit the data just as well.

We agree with the feedback of the Reviewer and we modified the corresponding paragraph in the revised version of the manuscript (lines 175-179). It is clear that taking a single individual O 1s peak, does not allow the exact identification of the different contributions. However, in this HAXPES study, we successfully employed the correlation of the fitted components as a function of the excitation energy (i.e. as a function of the information depth) to validate presence and depth evolution of the oxide and hydroxide species.

7. I realise space is short but it would be nice to see some 10 keV spectra for comparison with the lower energy ones.

10 keV spectra have now been included in the Letter (see Fig. 1). Please note that the high resolution spectra collected at 10 keV and reported in Fig 1 do not belong to the same electrochemical experiment and surface preparation, as the spectra pertaining to 6 keV. Typically, the high excitation energies were only used systematically for the analysis of the thicker passive

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layers. We ask the Editor/Reviewer for understanding that the collection of high resolution spectra is very beamtime consuming and therefore could not be performed for all the surface treatments/all the samples.

Appendix

Binding Energy assignment for the spectra of electrochemically treated Al-Cr-Fe CMAs

Core Level	Designation	BE (eV)	Chemical Shift (eV)	FWHM (eV)	Lineshape CasaXPS
Au4f$_{7/2}$	metal	84.0	-	0.6	A(0.1,0,400)SGL(100)
Al 2s	metal	118.0	-	1.2	SGL(50)
Al 2s	Al oxide	119.6	+ 1.6	1.5	SGL(70)
Al 2s	Al hydroxide	120.7	+ 2.7	1.3	SGL(70)
Al 2s	Al (sulfate component due to sulfuric acid esposure)	122.3	+ 4.3	1.5	SGL(100)
Al 1s	metal	1559.3	-	1	SGL(50)
Al 1s	oxide	1560.9	+ 1.6	1.7	SGL(30)
Al 1s	hydroxide	1561.9	+ 2.6	1.7	SGL(30)
Al 1s	Al (sulfate component due to sulfuric acid esposure)	1563.8	+ 4.5	1.7	SGL(50)
Cr 2p$_{3/2}$	metal	574.2	-	1.3	A(0.4,0.5,10)*GL(70)
Cr 2p$_{3/2}$	Cr_2O_3	576.8	+ 2.6	1.8	SGL(60)

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Cr $2p_{3/2}$	$Cr(OH)_3$	578.2	+ 4.0	1.8	GL(0)
Cr $2p_{3/2}$	CrO_3 or Cr sulphate	579.7	+ 5.5	1.7	GL(30)
Fe $2p_{3/2}$	metal	706.9	-	0.6	A(0.5,1,10)SGL(40)
O 1s	Cr oxide	531.3	-	1.5	SGL(30)
O 1s	Al oxide and Cr hydroxide (overlapping)	532.5	-	2.0	GL(30)
O 1s	Al hydroxide	534.0	-	1.9	GL(30)

Table A1: Assignment for the species present in the passivation layers of Al-Cr-Fe CMAs after electrochemical treatment in sulphuric acid at pH1 (excitation energy 2.3 keV, no post- monochromators used).

*b1. Urgency Statement

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Reference: Urgency statement

Dear Prof Compton

An urgent publication of the reported data is needed because a rapid communication is an ideal frame to present this new methodology characterisation concept because: i) it is of very broad interest to a larger scientific community in relation with electrochemical oxidation processes and ii) it can be used as reference in a growing field of synchrotron characterisation studies, iii) for the first time to our knowledge, the Al oxide and hydroxide spectral contribution have been unequivocally resolved.

The more detailed analysis and interpretation of the HAXPES data in terms of quantitative passive film composition determination will be published in form of a “full paper “ in a more specialised journal.

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Zürich, 27th February 2014

Best Regards,

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Highlights

- HAXPES characterisation of electrochemical passivation layers for Al-Cr-Fe CMA's.
- Oxide and hydroxide signals identified for Al 2s/Cr 2p photoelectron core levels.
- Shallow and deep core levels analysed to achieve diverse surface sensitivity.
- Cr 18% at concentration threshold necessary for stable passivation at pH 1 H_2SO_4.
- X-ray energy variation for cations and hydroxide/oxide distribution identification.

*c. Manuscript
Click here to view linked References

1 # Hard X –Ray Photoelectron Spectroscopy (HAXPES) characterisation of
2 electrochemical passivation oxide layers on Al-Cr-Fe Complex Metallic Alloys
3 (CMA)

4

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27

Abstract

A Hard X-Ray Photoelectron Spectroscopy (HAXPES) characterisation of the passivation layers formed by electrochemical polarisation of corrosion resistant Al-Cr-Fe complex metallic alloys (CMAs) is presented. Employing a large range of X-ray excitation energies from 2.3 to 10.0 keV allowed identifying (by cross-correlating results of different excitation energies) and resolving the depth distributions of Al- and Cr- oxide and hydroxide species in the (Al,Cr)-passive layer through the whole film thickness, down to the oxide- alloy interface. Simultaneous analyses of the shallow Al 2s and deep Al 1s core level lines (which are more bulk- and surface-sensitive, respectively) provided complementary information to effectively resolve the relative contributions of hydroxide and oxide species as a function of depth below the surface. The Cr threshold concentration necessary to obtain passive film stabilisation at pH 1 was found to be 18 (at %).

Keywords

Electrochemical passivation, Hard X-Ray Photoelectron Spectroscopy (HAXPES), Al alloys, Complex Metallic Alloys, composition depth profiling, oxide/hydroxide.

1. Introduction

Al-Cr-Fe complex metallic alloys (CMA) are intermetallic phases occurring as crystalline approximants of quasicrystals [1]. The Al-Cr-Fe CMA phases present peculiar bulk [2] and surface properties such as low friction, hydrophobicity and high corrosion resistance in the 0-14

53 pH range [3-6], being good candidates as multifunctional corrosion protecting coatings. Their
54 corrosion resistance in very aggressive environments, such as acidic sulphuric or chloride
55 containing electrolytes, has been proven by electrochemical techniques [3, 7]. The formation of a
56 6-8 nm thin protective passive layer composed of several Al and Cr oxyhydroxide stacks was
57 evidenced by X-ray Photoelectron Spectroscopy (XPS) [3, 8] and complementary XPS and Auger
58 sputtering depth profile analyses, which are typically used to determine the depth-resolved
59 chemical constitution of layers with a thickness exceeding the XPS information depth. However,
60 the main disadvantages of the latter techniques are the possible preferential sputtering effects and
61 the need for an accurate calibration of the sputtering rate [9]. Investigation of the oxidation
62 mechanism of an alloy not only requires detailed information on the chemical constitution of the
63 growing oxide, but also on the oxidation-induced changes in the alloy adjacent to the alloy/oxide
64 interface [10]. Unfortunately, the information depth obtained by angle resolved XPS analysis
65 using a conventional Al- or Mg- X-ray source is limited up to about 6 nm and therefore cannot
66 probe the alloy/oxide interface for 'thicker' passive oxide layers as formed by e.g.
67 electrochemical polarisation [10]. Furthermore, the energy resolution of standard laboratory set-
68 ups is typically insufficient to unequivocally resolve the oxide and hydroxide components in the
69 measured Al 2s, Al 2p, Cr 2p spectra of oxidised Al-Cr alloys [11].

70 The present study demonstrates that Hard X-ray XPS (HAXPES) is a very powerful
71 technique to characterise relatively thick electrochemically formed passive layers, as grown on
72 Al-Cr-Fe CMAs after potentiostatic anodic polarisation. By tuning the energy of the incident X-
73 rays up to 10 keV [12, 13], HAXPES can effectively probe the chemical constitution as a
74 function of depth over the entire passive layer and across the reacting alloy/oxide interface. In
75 addition, the use of a synchrotron source with monochromatised X-ray optics provides an
76 enhanced energy resolution as compared to conventional laboratory XPS set-ups and allows

77 simultaneous analysis of shallow and deep core-level photoelectron lines (like Al 2s and Al 1s),
78 thereby opening the field to new physics. As demonstrated in this work, use of high-energy
79 resolution at various excitation energies is essential for resolving the chemical environments in
80 the disordered, multi-element oxyhydroxide layers formed by electrochemical treatments, where
81 a direct comparison with known reference oxide and/or hydroxide bulk compounds is not
82 possible.
83

84 ## 2. Experimental Details

85 ### *2.1 Materials and electrochemical treatment*

86 Four Al-based CMA intermetallics, namely the orthorhombic $Al_{78.8}Cr_{15.5}Fe_{5.7}$ and
87 $Al_{79.12}Cr_{17.76}Fe_{3.12}$, the hexagonal $Al_{78.7}Cr_{20.6}Fe_{0.7}$ and the cubic $Al_{64.2}Cr_{27.2}Fe_{8.1}$ (at %) phases
88 were investigated. The first three single crystals were prepared at LMU (Munich) [14], while the
89 polycrystalline gamma phase was grown at LSGMM (Ecole des Mines, Nancy).
90 All the samples were polished to mirror finish using diamond paste and ethanol and
91 electrochemical anodically potentiostatic polarised in the low passive domain at 0 V_{SCE} for 24 h
92 in sulphuric acid electrolytes at pH 0 or 1 using a conventional three electrode cell in absence of
93 deareation.
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95

96 ### *2.2 HAXPES measurements*

97 The measurements were conducted at the ID32 beamline of the European Synchrotron Radiation
98 Facility (ESRF). The excitation energy was varied from 2.3 to 10.0 keV. A double-crystal
99 Si(111) monochromator and a PHOIBOS 225 HV hemispherical electron analyser [15] were used
100 to record HAXPES spectra at various electron take-off angles with respect to the sample surface.

101 Selected high resolution measurements were performed using additional Si(333) and Si(555)
102 post-monochromators. The binding energy (BE) was calibrated to the Fermi energy of gold.
103 CasaXPS (2009 Casa Software Ltd) was used for data analysis applying a Shirley-type
104 background and asymmetric lineshapes for the metallic peaks and Gaussian/Lorentzian ones for
105 the oxidic ones. The lineshapes of the metallic peak components have been determined from the
106 spectra of clean alloy samples. Due to the variation of the energy resolution with the excitation
107 energy (different source/analyser resolution, use of post-monochromators), the lineshape
108 parameters of the fitted metallic and oxidic components differ in some cases. The analyser
109 transmission function was provided by SPECS GmbH.

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111

112 3. Results and Discussion

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114 Fig. 1 displays exemplary HAXPES spectra of the Al 2s, Al 1s and Cr $2p_{3/2}$ core levels recorded
115 at 6.0 and 10.0 keV for $Al_{78.7}Cr_{20.6}Fe_{0.7}$ after electrochemical potentiostatic polarisation in pH 1
116 (sulphuric acid), applying $0V_{SCE}$ for 24 hours on two different surface treatments: metallographic
117 polishing without and with sputter/annealing for 6 and 10 keV, respectively. For all specimens
118 studied, no oxidised state of Fe could be detected in the measured Fe $2p^{3}{}_{/2}$ core-level spectra;
119 hence we conclude that Fe does not contribute to the formation of the passivation layer.
120 At least two main oxidic components are identified in the measured Al 2s spectra positioned at
121 shifts of +1.6 and +2.7 (± 0.1) eV with respect to the metallic peak. They can be attributed
122 respectively, to Al-oxide and Al-hydroxide environments that are expected to form during
123 electrochemical aqueous oxide formation. Such components were also identified in the measured
124 Al 1s spectra at relative chemical shifts of +1.6 and +2.5 (± 0.1) eV with respect to the metallic

125 peak. Fig. 1a-b shows that the Al 1s photoelectron line, with a much higher BE, provides an
126 enhanced surface sensitivity as compared to the Al 2s line. Consequently, due to the enhanced
127 degree of hydroxylation near the surface, the relative contribution of the hydroxide peak is much
128 more pronounced in the measured Al 1s spectra. The Cr $2p_{3/2}$ oxidic spectra (see Fig. 1c,d) can
129 also be described by at least one oxide and one hydroxide component with a respective chemical
130 shift of + 2.6 and + 4.0 (± 0.1) eV, in accordance with Ref. [16].

131 Thus HAXPES analysis with a high energy resolution can well resolve the different local
132 environments around core-ionised Al and Cr cations in an oxide and hydroxide (ligand)
133 environment in these defective (Al,Cr)-oxyhydroxides . However, due to the high degree of local
134 disorder, the local coordination spheres (e.g. bond length, angle and ligand-type) of the Al and Cr
135 atoms in an oxide and hydroxide environments vary. This results in a relative large intrinsic
136 width of the resolved oxide and hydroxide components (as compared to metallic component)
137 which cannot be improved by further increase of the energy resolution of the HAXPES analysis.
138 This can also explain the very high BE of the defective and disordered hydroxides.

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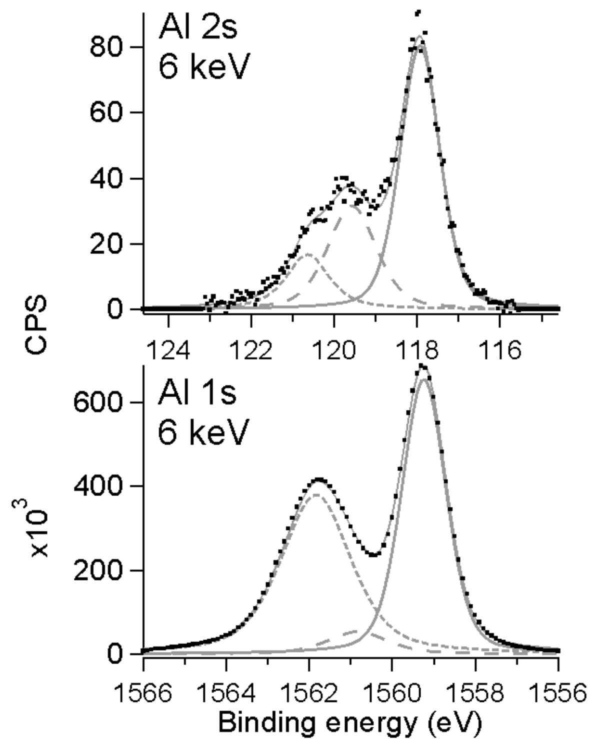
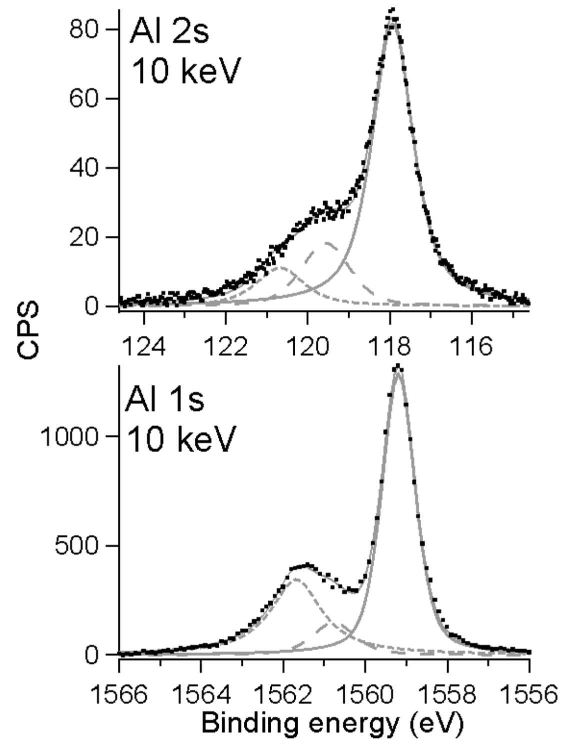
149 a) b)





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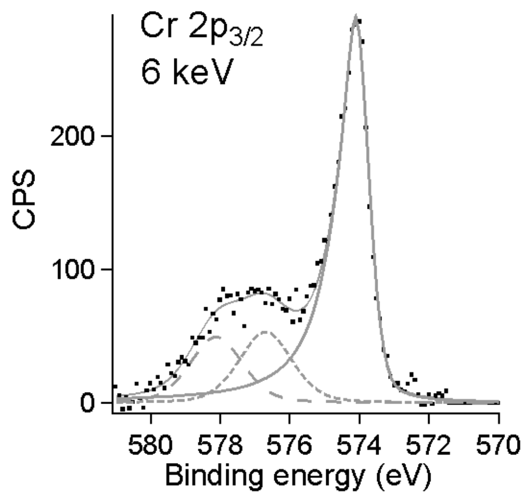
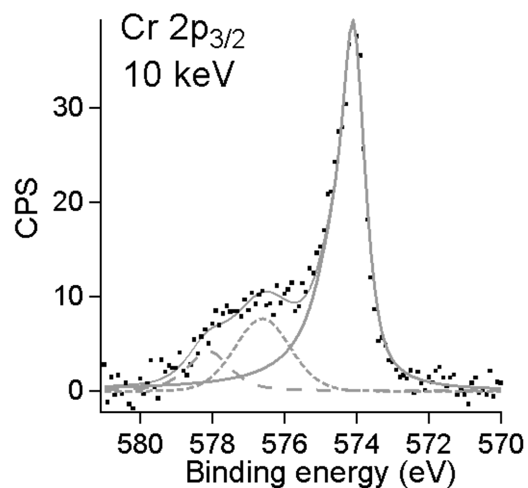
151 c) d)





152

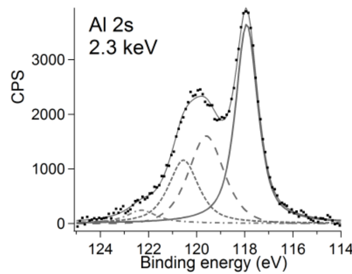
153 **Fig. 1.** Reconstructed high-resolution Al 2s, Al 1s and Cr $2p_{3/2}$ core-level spectra recorded at 6

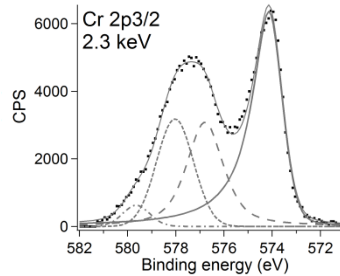
154 and 10 keV for the electrochemically polarised surface of $Al_{78.7}Cr_{20.6}Fe_{0.7}$ alloy in sulphuric acid

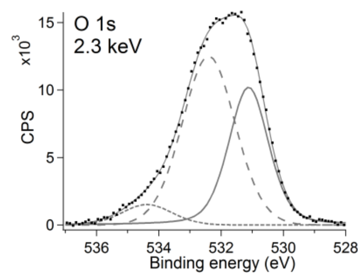
155 pH 1, applying $0V_{SCE}$ for 24 hours on two different initial surface preparations.

156

157 **a)** **b)** **c)**







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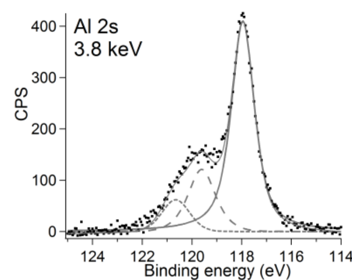
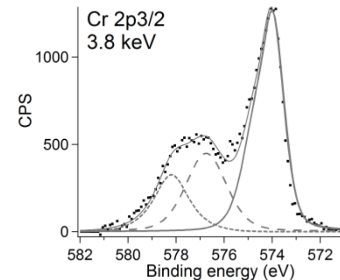
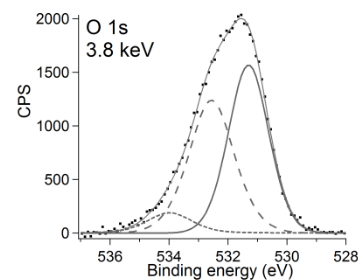
159 **d)** **e)** **f)**







160

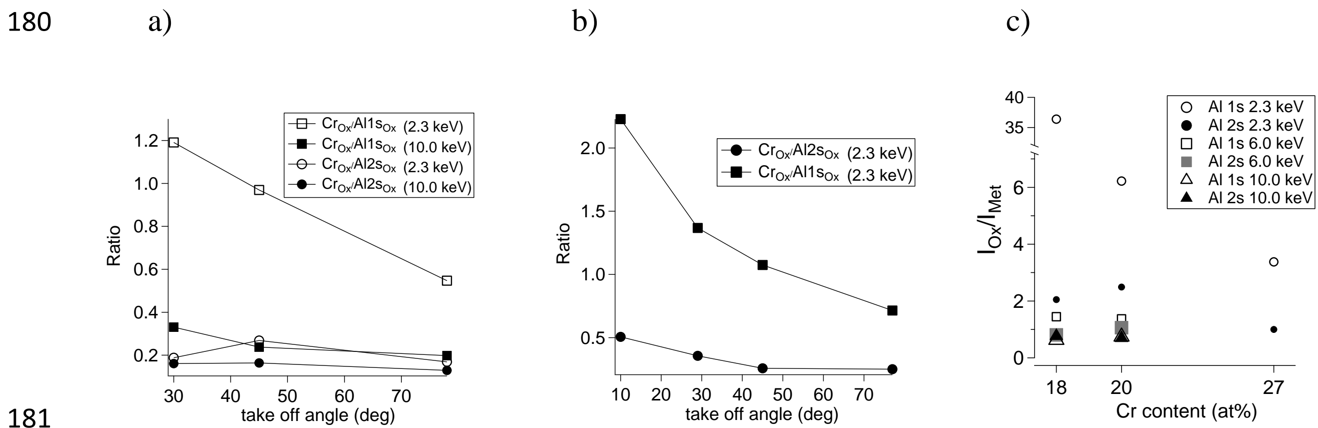
161 **Fig. 2.** Reconstructed Al 2s, Cr $2p_{3/2}$ and O 1s core-level spectra for the electrochemically
162 polarised surface of $Al_{64.2}Cr_{27.2}Fe_{8.1}$ alloy for 24 hours in sulphuric acid (pH 0) at $0V_{SCE}$ recorded
163 at 45 deg. take-off angle.

164

165 Evaluation of the recorded HAXPES spectra as a function of the excitation energy allowed a non-
166 destructive, depth-resolved determination of the chemical constitution of the passivation layer.
167 The Al 2s and Cr $2p_{3/2}$ spectra (Fig. 2) recorded at 2.3 keV and 3.8 keV for the $Al_{64.2}Cr_{27.2}Fe_{8.1}$
168 alloy confirm the incorporation of both Al and Cr in the grown oxyhydroxide passivation layers
169 with an enhanced degree of hydroxylation towards the outer surface. For low excitation energies
170 (i.e. more surface-sensitive), an additional minor component appears in the Al 2p and Cr 2p
171 spectra, which is attributed to the presence of small amount of sulphate species at the outer
172 surface (originating from the used sulphuric acid). The O 1s recorded at different excitation
173 energies could be described by three components at 534.0 eV, 532.5 and 531.3 eV attributed to a

174 Al hydroxide, the overlapping Al oxide and Cr hydroxide and Cr oxide environment,
175 respectively[17]. Due to the large intrinsic width of the O 1s line, working at an increased energy
176 resolution did not help to reduce the overlap of the oxide and hydroxide components in the O 1s
177 peak envelope. Nevertheless, the distribution of the O 1s oxide and hydroxide (on the surface) as
178 a function of depth below the surface was clearly evidenced from the excitation-energy-
179 dependent analysis.

180 a) b) c)



181

182 **Fig. 3.** Intensity ratios at different excitation energies and electron take-off angles for **a)** the
183 Cr20% alloy after 24 hours in sulphuric acid (pH 1) at $0V_{SCE}$, **b)** the Cr27% alloy after 24 hours
184 in sulphuric acid (pH 0) at $0V_{SCE}$ and **c)** Al intensity ratios as a function of the alloy Cr content
185 after 24 hours in sulphuric acid (pH 1) at $0V_{SCE}$. Estimated error ±10%.

186

187 For the Al-Cr-Fe phases, passivation is ensured by the formation of the complex (Al,Cr)
188 oxyhydroxide film, as outlined above. The resolved Cr_{oxide}/Al_{oxide} intensity ratios (taking the sums
189 of the oxide and hydroxide components for each core level) evidence that the oxyhydroxide
190 layers are richer in Cr towards their outer surface (Fig. 3a-b). On this basis, the average
191 thicknesses of the passivation layers for the electrochemically treated Al-Cr-Fe phases can be
192 estimated by assuming a simplified bilayer structure [18], consisting of an Al-oxyhydroxide
193 bottom layer adjacent to the metal/oxide interface and a Cr-oxyhydroxide top layer adjacent to

194 the surface. Table 1 reports these thickness estimations using the intensity attenuations of the

195 HAXPES Cr $2p_{3/2}$ and Al 2s signals recorded at 6 keV (atomic densities of 51, 47 and 41 at/nm^3

196 were used for the alloy, Al_2O_3 and Cr_2O_3, respectively [11]). As shown in Fig. 3c), the lower the

197 Cr content, the thicker the oxyhydroxide film, thus indicating higher ionic mobility (presence of

198 defects) and therefore a poorer corrosion resistance. The Cr 17.76 and 20.6 at% phases present

199 similar oxide thicknesses, thus confirming that the Cr threshold for the formation of a barrier-type

200 passivation layer in pH 1 sulphuric acid requires a minimum Cr content > 18 at% in the alloy, in

201 accordance with previously published electrochemical current transient measurements [7].

202

Composition (at%)	**Cr oxide calculated thickness (nm)**	**Al oxide calculated thickness (nm)**
$Al_{78.8}Cr_{15.5}Fe_{5.7}$	2.1	11.0
$Al_{79.12}Cr_{17.76}Fe_{3.12}$	1.0	4.4
$Al_{78.7}Cr_{20.6}Fe_{0.7}$	0.9	5.6

203

	Calculated IMFP (Å) in Al_2O_3	
	2.3 keV	**10 keV**
30 deg	**Al1s** 9.7 **Al2s** 22.5 **Cr 2p** 18.6	**Al1s** 69.0 **Al2s** 79.0 **Cr 2p** 75.8

78 deg	**Al1s** 18.9	**Al1s** 134.0
	Al2s 43.6	**Al2s** 153.2
	Cr 2p 36.1	**Cr 2p** 147.1

204 **Table 1.** Oxide thickness estimation using equations in [18] and IMFP inAl_2O_3 at various
205 excitation energies and angles according to [19].

206

207

208

209

210 ## 4. Conclusions

211

212 HAXPES was used to perform a non-destructive depth profile analysis of the passivation layer
213 formed on new corrosion resistant Al-Cr-Fe complex metallic alloys after electrochemical
214 polarisation in very acidic aggressive electrolytes (sulphuric acid pH 1 or 0).
215 It is demonstrated that HAXPES provides a powerful tool to unveil the in-depth chemical
216 constitution of relatively thick oxyhydroxide layers. The present letter emphasised qualitatively
217 the new methodology.
218 - Analysis of core-level photoelectron spectra recorded at progressively increasing X-Ray
219 excitation energies revealed: (i) the hydroxide and oxide distributions as a function of
220 depth and (ii) the enrichment of Cr cations towards the outer layer surface.
221 - Using Hard X- rays, deep core-level photoelectron lines, which cannot be excited with
222 conventional laboratory X-ray sources were collected (i.e. Al 1s). The shallow and deep
223 core levels provided complementary information, i.e. the Al 1s signal allowed an

enhanced surface sensitivity especially at 2.3 keV, evidencing with the help of Cr_{ox}/Al_{ox} signal ratios that Cr oxyhydroxide is concentrated towards the outer film surface.

- A simple 2-layered Cr and Al oxide model was adopted to estimate the thickness of the passivation layers. For this purpose, high excitation energies were used to probe the interface and to record a reliable photoelectron metallic signal of the substrate.
- Combined angle and energy-resolved experiments allowed the determination of a Cr concentration threshold of 18at % Cr for the formation of a thin protecting barrier-type passive layer.

Acknowledgements

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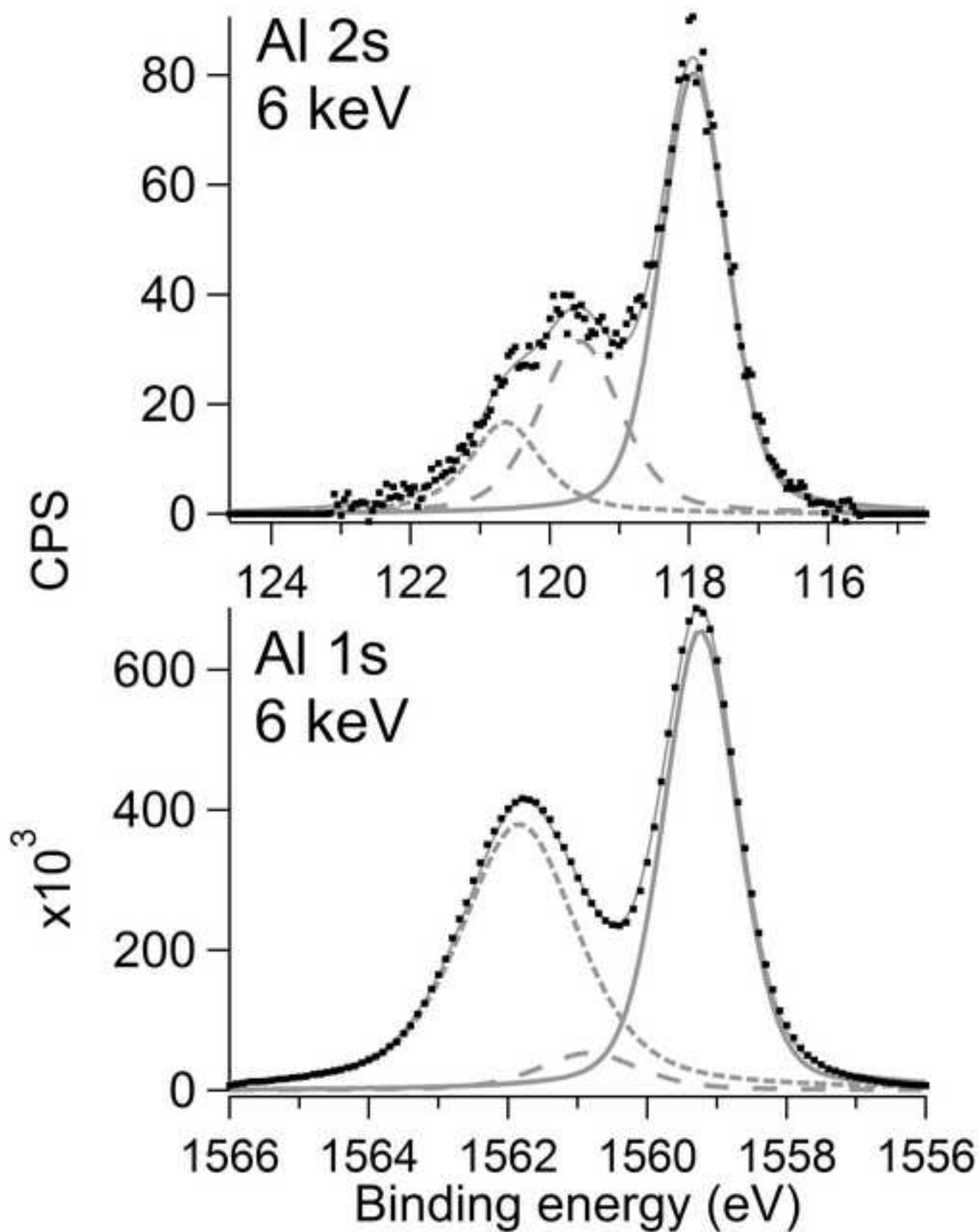

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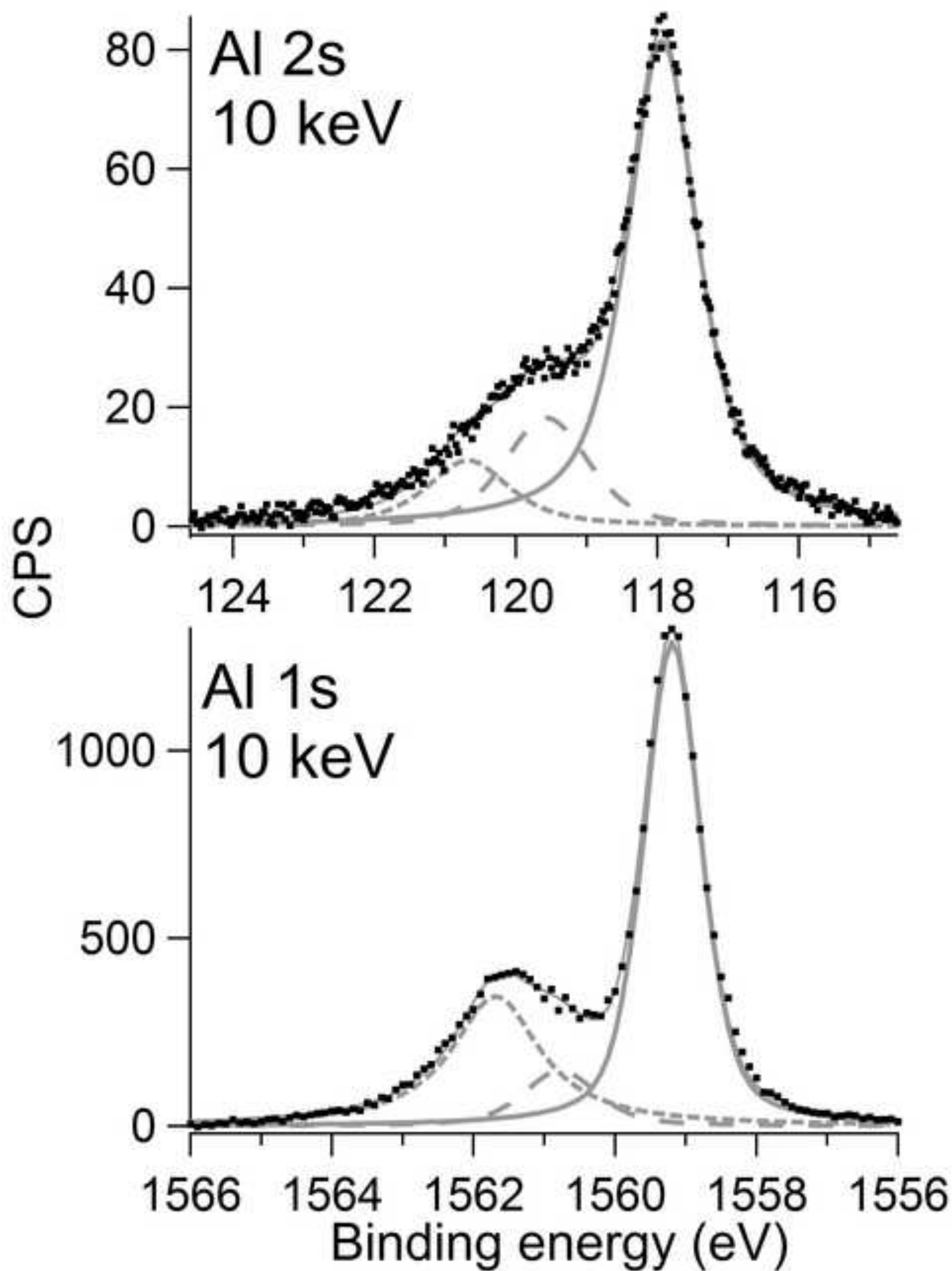

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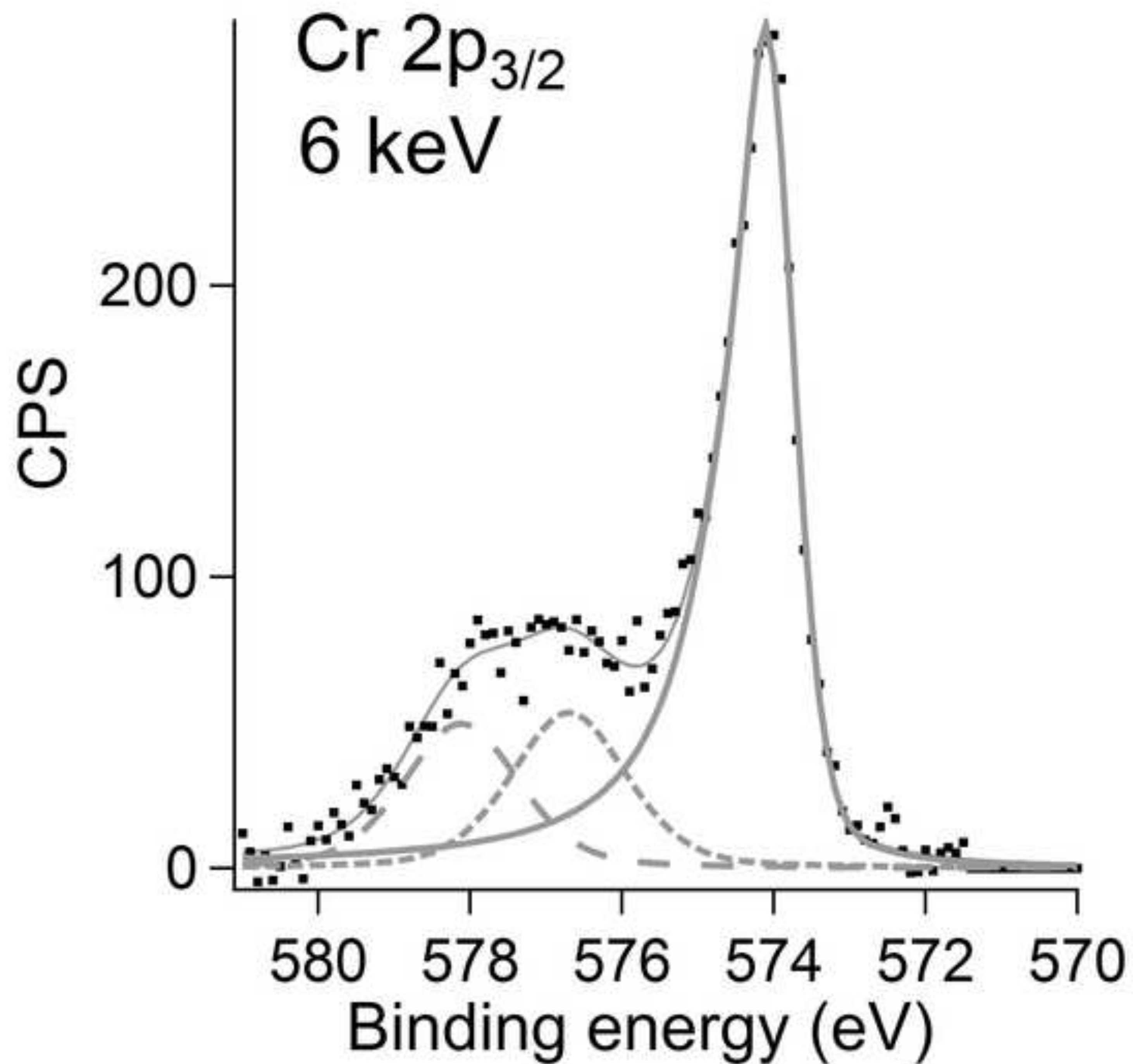

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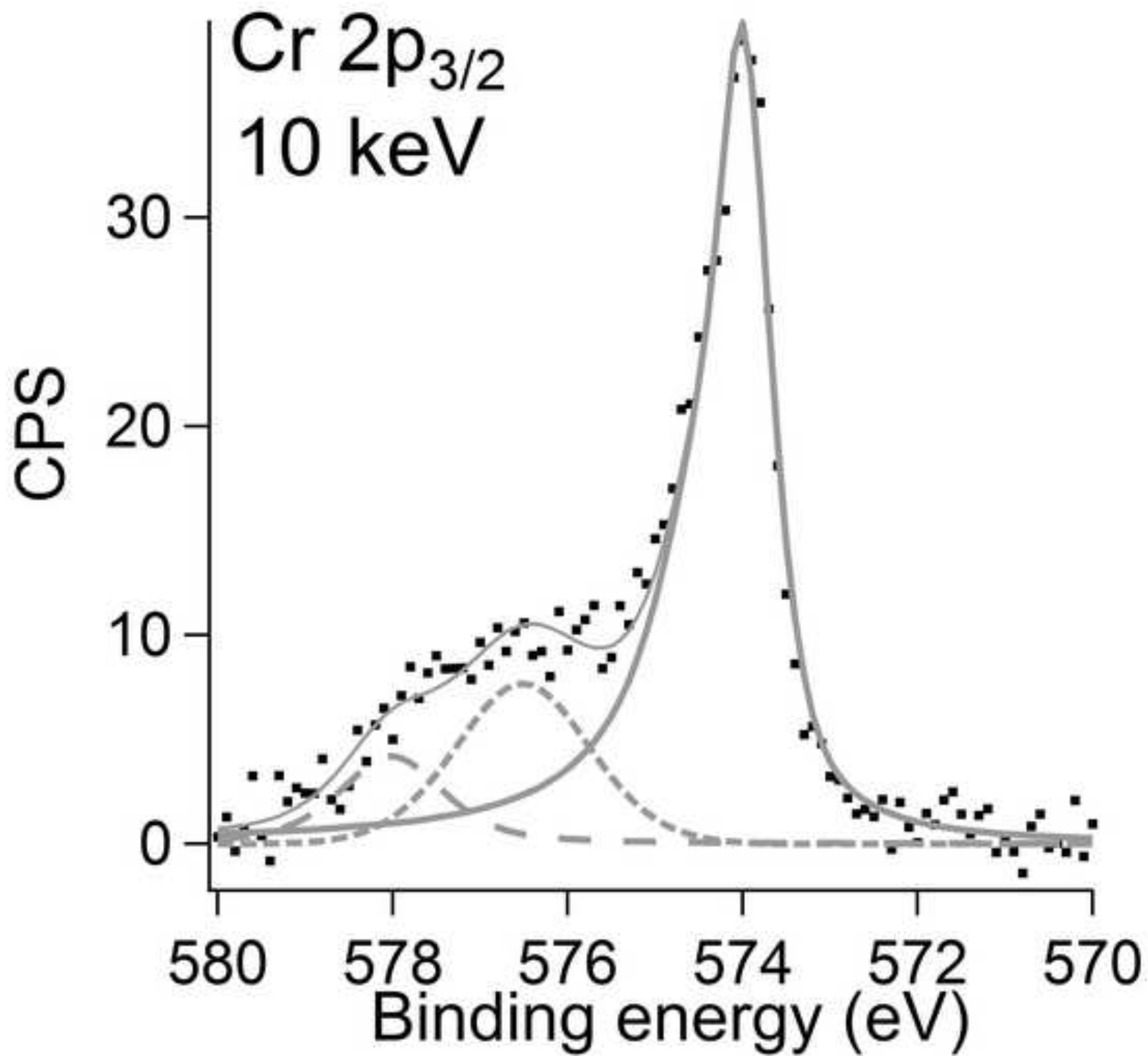

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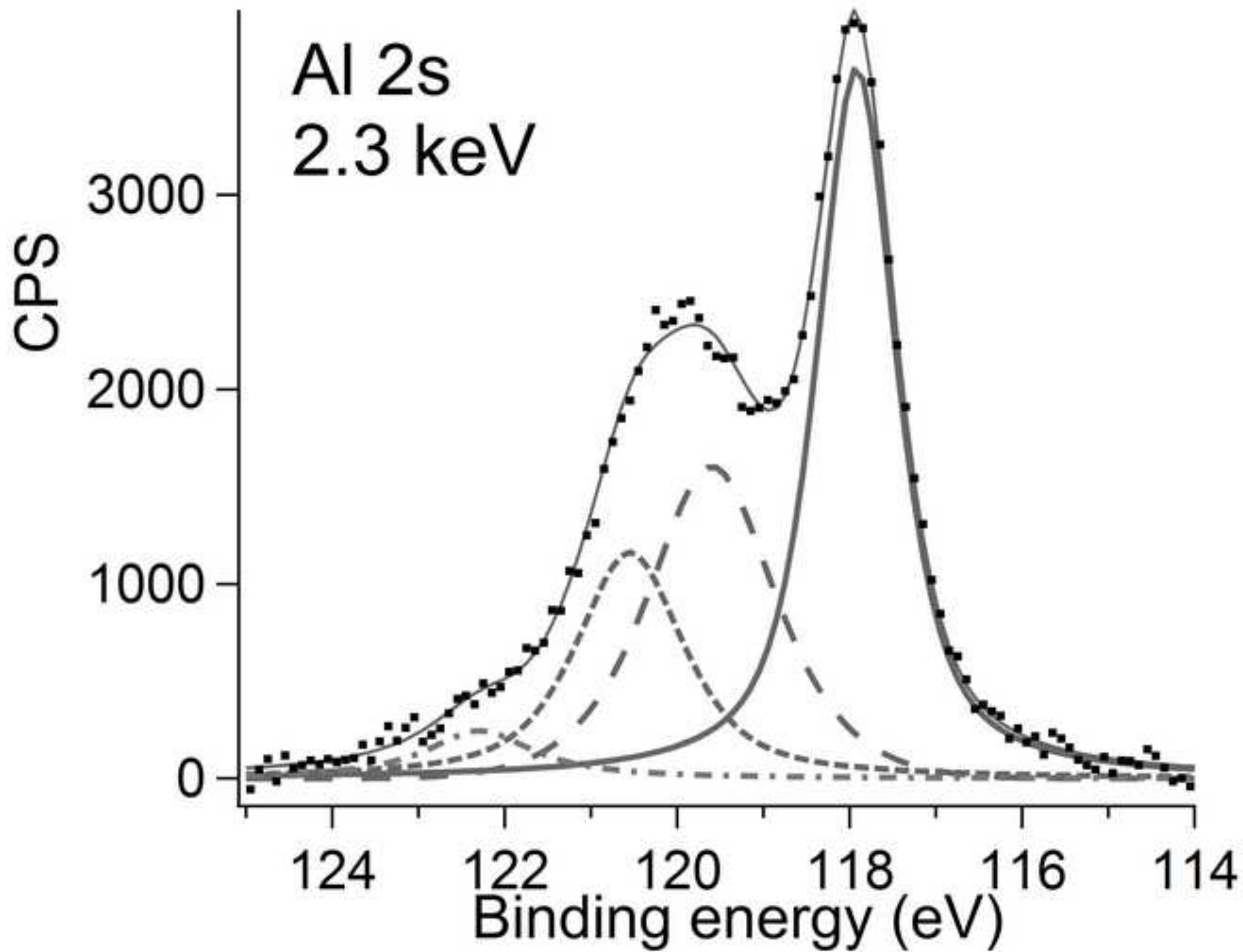

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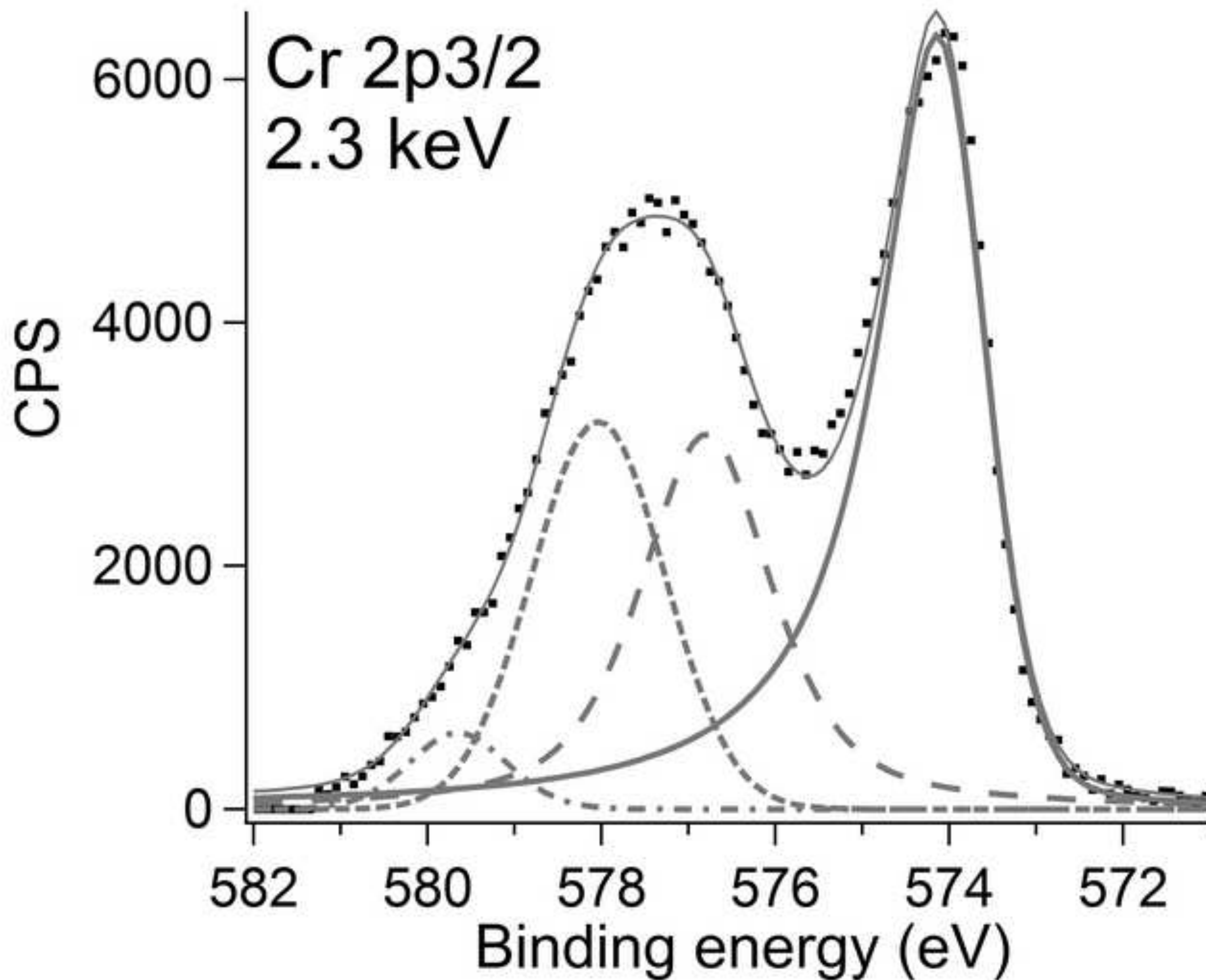

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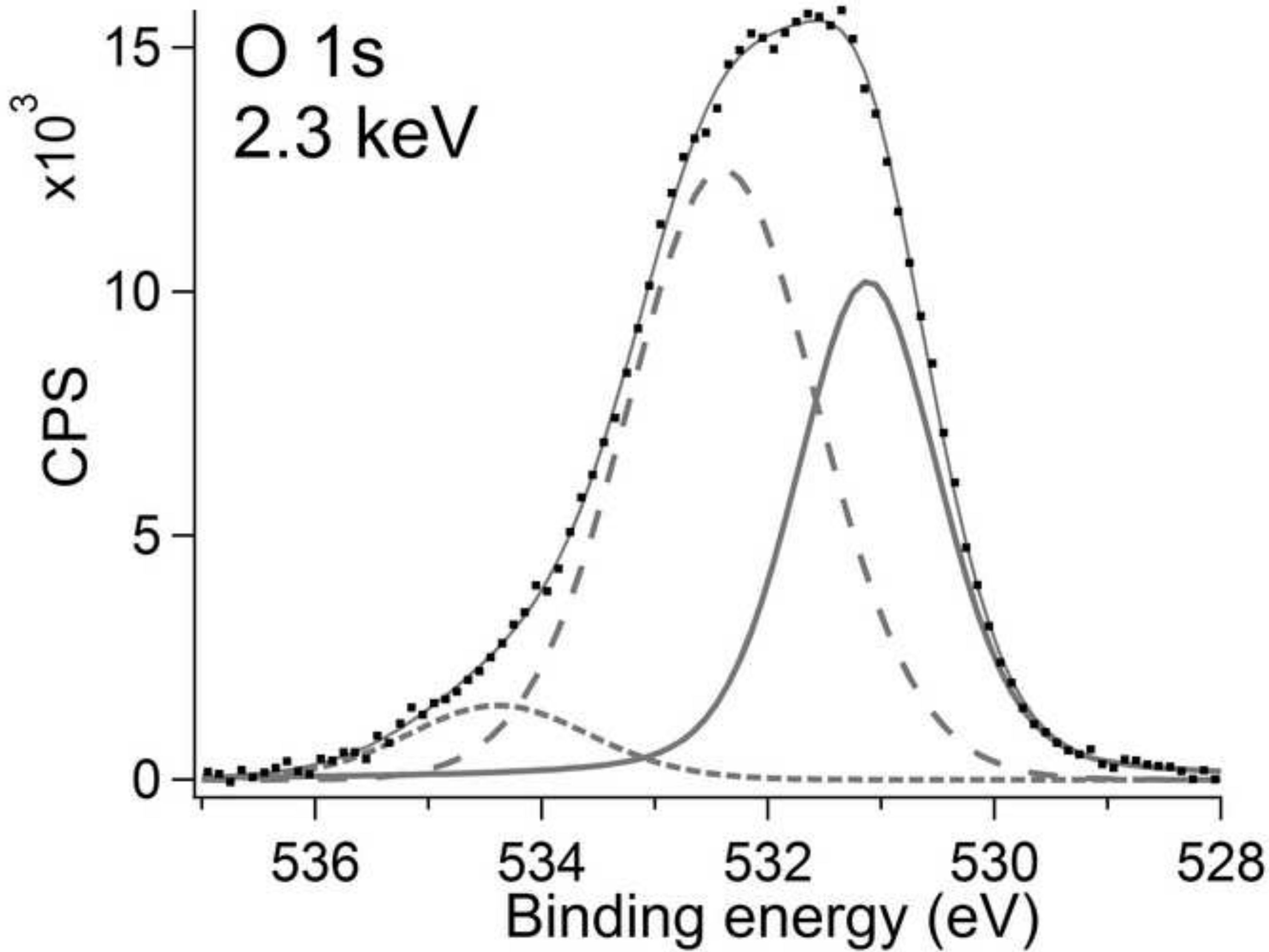

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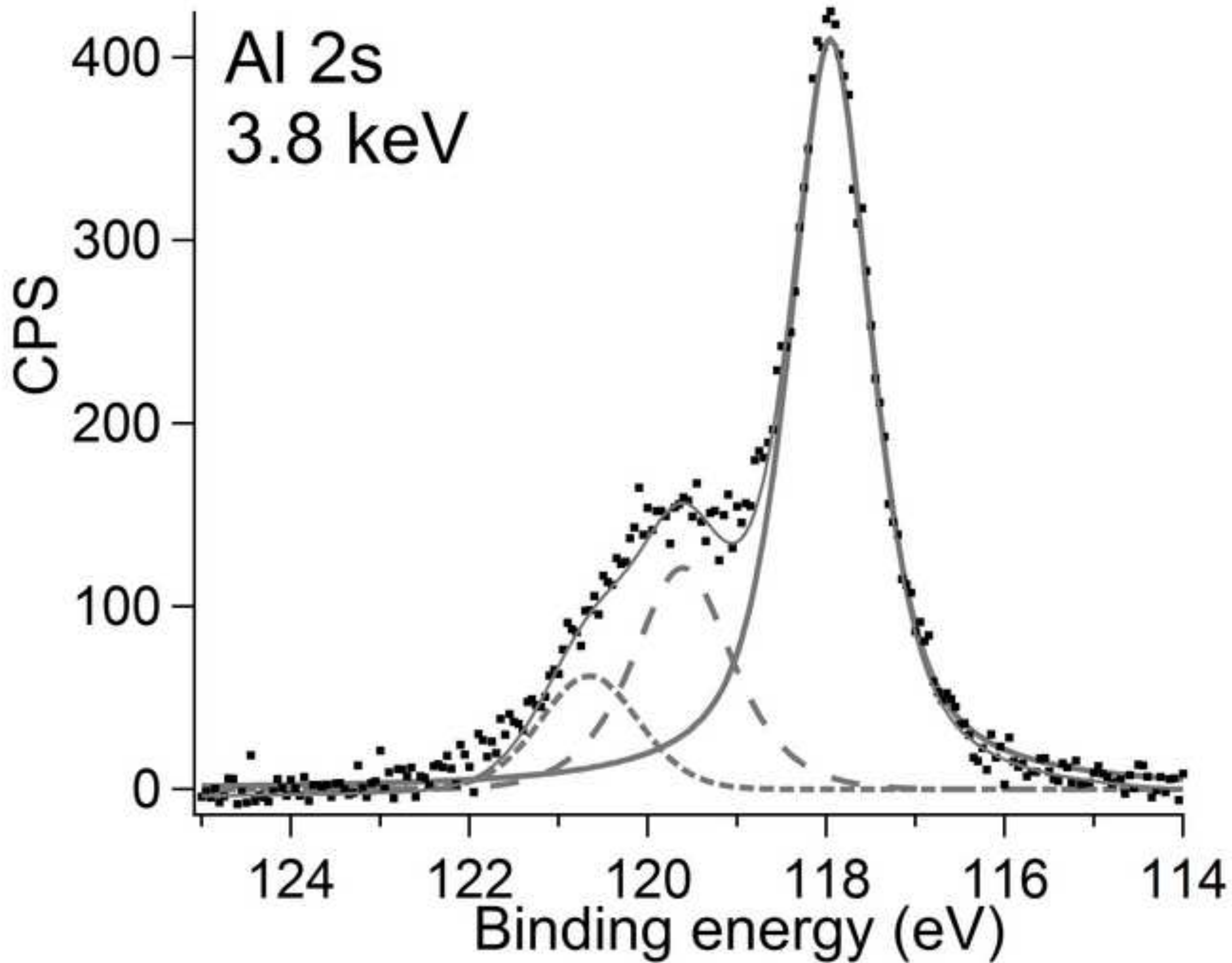

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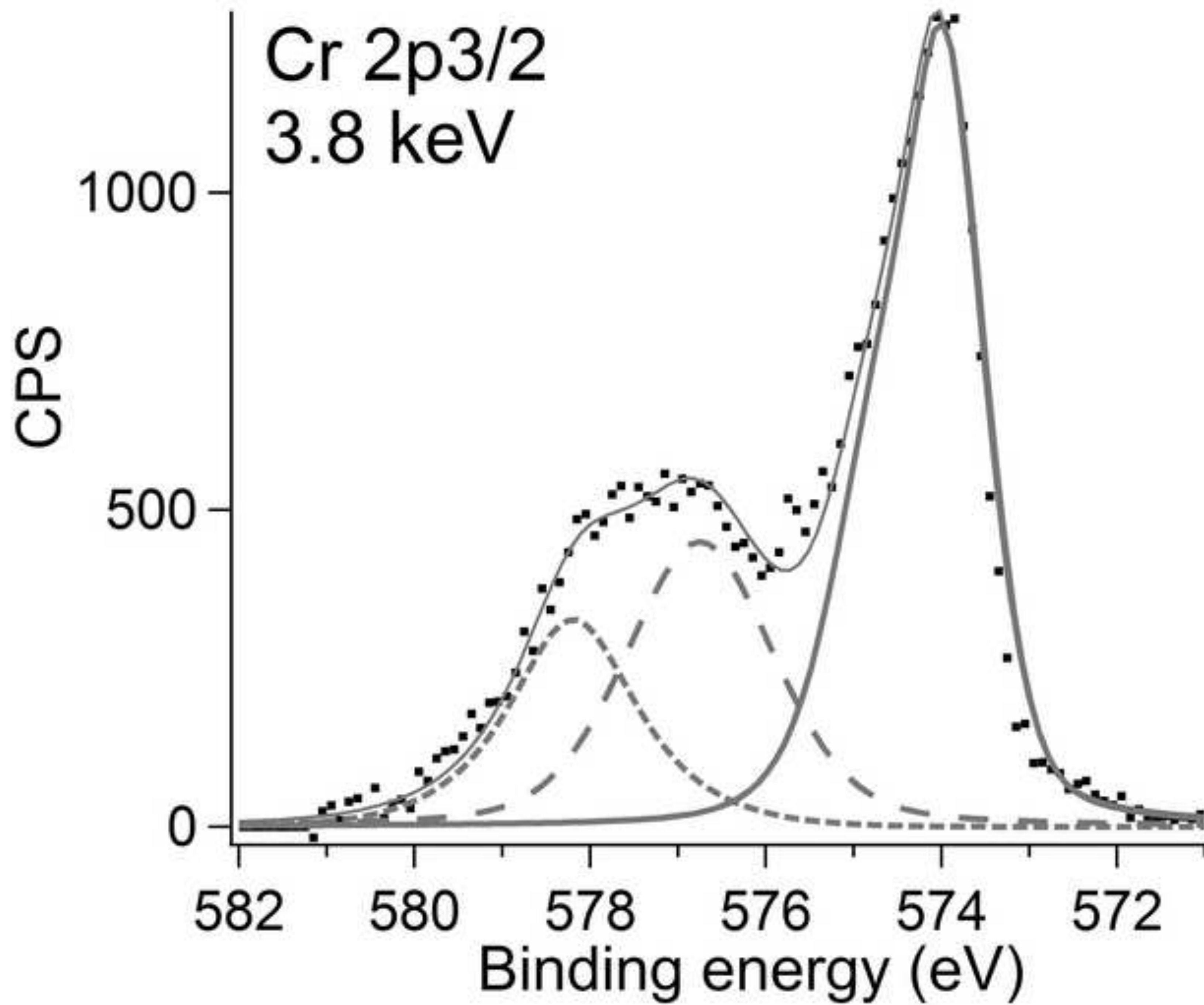

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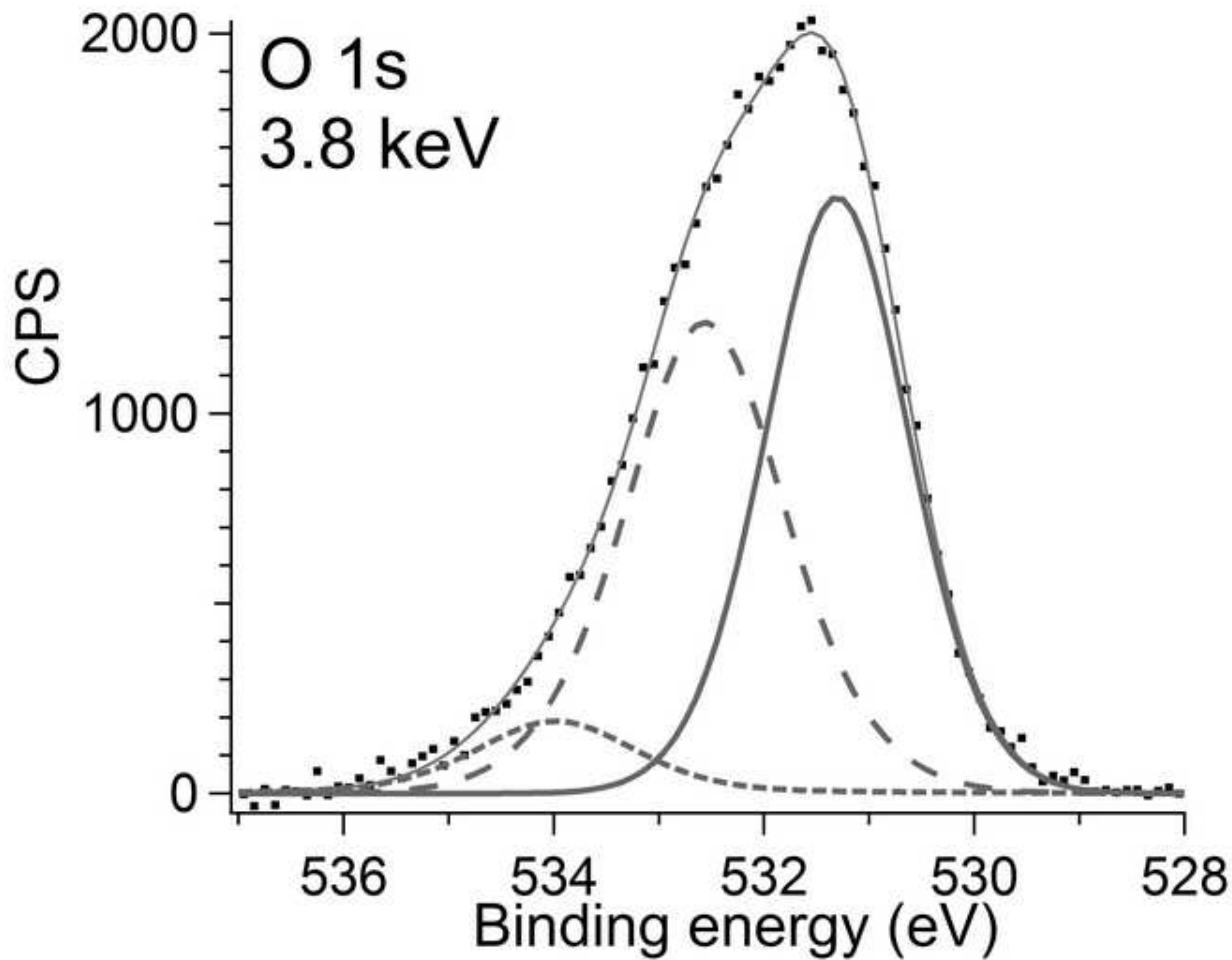

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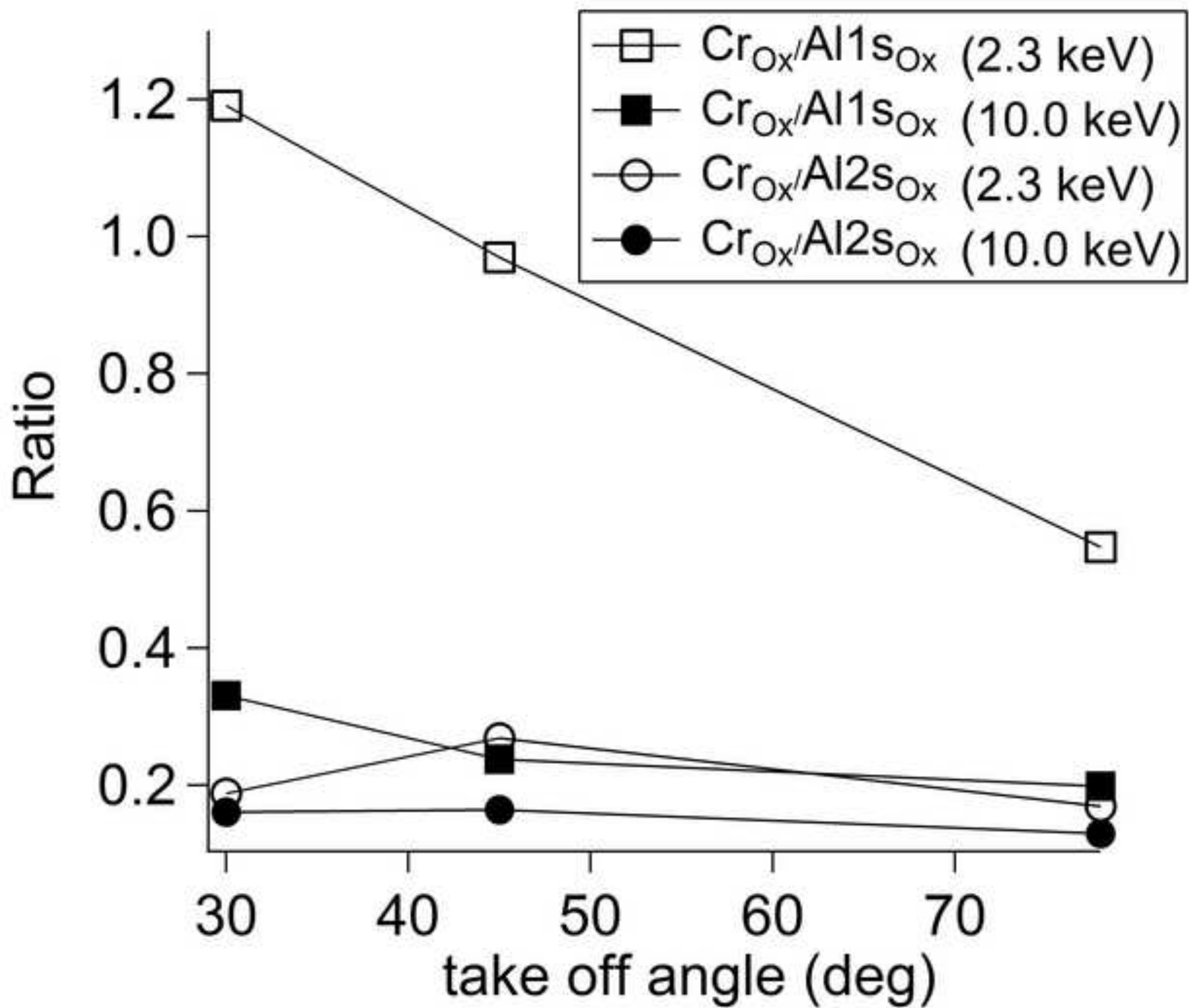

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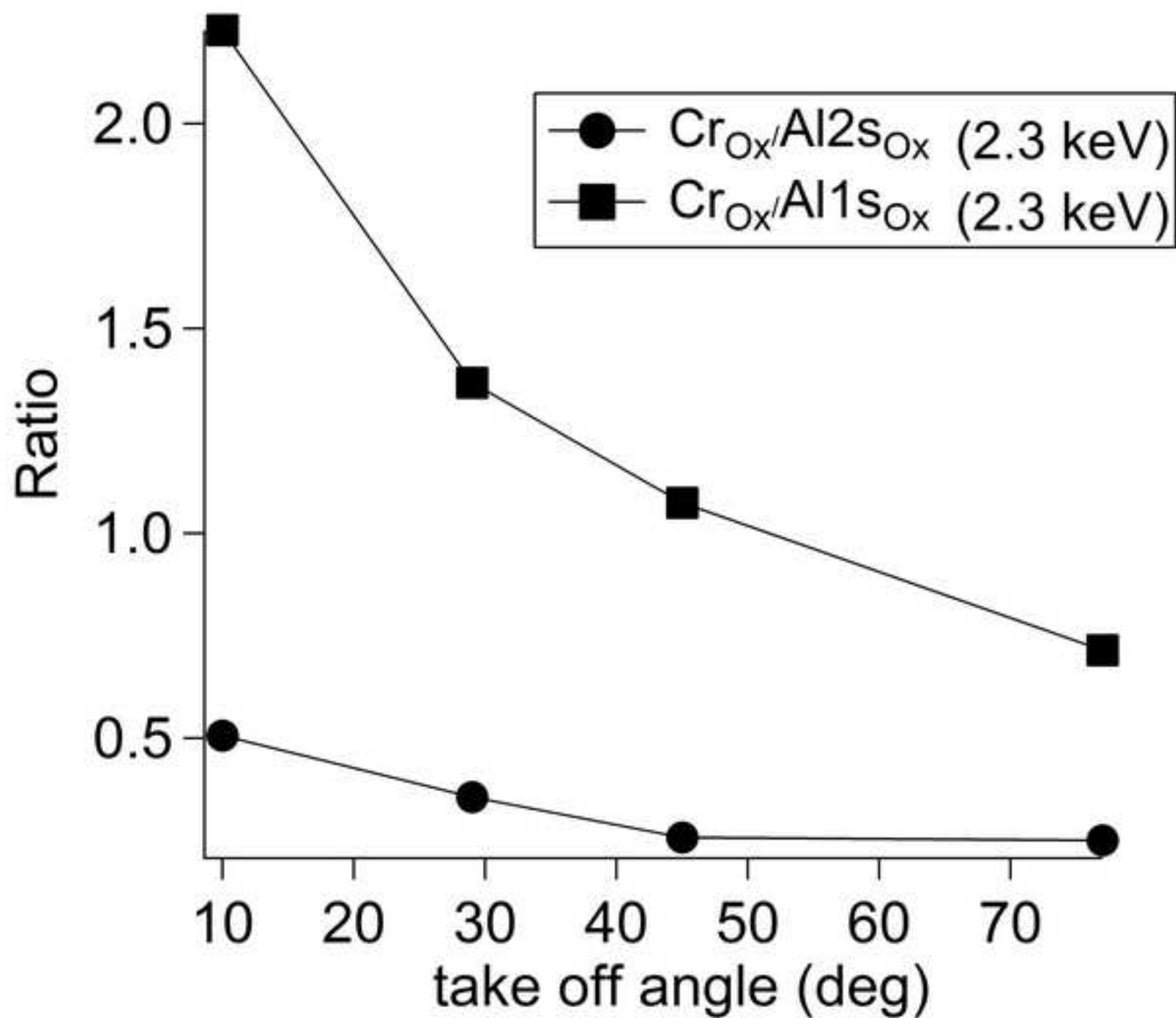

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