XPS characterisation of in situ treated lanthanum oxide and hydroxide using tailored charge referencing and peak fitting procedures

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\section*{A B S T R A C T}

A technique is described for deposition of gold nanoparticles under vacuum, enabling consistent energy referencing of X-ray photoelectron spectra obtained from lanthanum hydroxide La(OH)\textsubscript{3} and in situ treated lanthanum oxide La\textsubscript{2}O\textsubscript{3} powders. A method is also presented for the separation of the overlapping lanthanum 3d and MNN peaks in X-ray photoelectron spectra acquired with Al K\textalpha\ radiation. The lower satellite intensity in La(OH)\textsubscript{3} compared to La\textsubscript{2}O\textsubscript{3} is related to the higher ionicity of the La–O bond in the former compared to the latter compound. The presence of an additional peak in the valence band spectrum of the hydroxide compared to the oxide is attributed to the O–H bond as indicated by density functional theory based calculations. A doublet in the O 1s peak of lanthanum oxide is associated to the presence of two distinct oxygen sites in the crystal structure of this compound.

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\section*{1. Introduction}

Lanthanum oxide has chemical and electronic properties that meet the requirements for applications in various fields. It is employed in catalysis for isomerisation and hydrogenation of olefins [1] and oxidative conversion of methane and ethane [2,3], as a high dielectric constant gate oxide in microelectronics [4–7] and as corrosion inhibitor on galvanised steel [8,9], aluminium [10] and magnesium alloys [11,12]. Lanthanum containing oxides have additional applications, for example as oxygen ion or proton conductors for solid oxide fuel cells SOFCs (e.g. La\textsubscript{10}(SiO\textsubscript{4})O\textsubscript{3} [13], LaGaO\textsubscript{3} [14], La\textsubscript{2}M\textsubscript{2}O\textsubscript{3} [15], LaNbO\textsubscript{4} and LaTaO\textsubscript{4} [16]), as mixed ionic-electronic conductors as electrode materials for SOFCs or for gas separation membranes (e.g. LaMnO\textsubscript{3}, LaCoO\textsubscript{3} [17] and La\textsubscript{2}NiO\textsubscript{4} [18]) or applications related to their magnetic and magnetoelastic properties (e.g. LaMnO\textsubscript{3} [19,20]). Lanthanum oxide can potentially be present as a secondary phase in these materials after precipitation, for example in cases of non-stoichiometry with excess of this element.

Lanthanum oxide reacts spontaneously with water vapour at room temperature and is hydrated in bulk to form lanthanum hydroxide [21,22]. For many of the cited applications the differentiation between lanthanum oxide and lanthanum hydroxide is of interest, especially for surfaces participating in chemical reactions. There are, however, only few studies where lanthanum oxide and hydroxide are compared directly with X-ray photoelectron spectroscopy (XPS) using the same instrumentation and experimental setup. The comparison of the spectra obtained in various studies is therefore difficult, as differences in X-ray radiation, analyser settings, charge referencing and data treatment procedures lead to differences in the results that are not related to the materials. Furthermore the sample preparation procedure is rarely mentioned although it affects the surface chemistry of these reactive materials. The few available studies where both compounds are compared concern thin films, produced at room temperature [23,24] and/or samples dehydrated by ion bombardment [24,25]; thus they will not necessarily have the same compositional or structural characteristics as the bulk materials.

Lanthanum photoelectron peaks in lanthanum compounds are known to show strong satellite peaks. The intensity and energy separation of the satellites relative to the main peak are highly sensitive to the ligand atoms. Charge transfer from the valence band of the ligand atom to the 4f\textsuperscript{6} orbital of the core ionised lanthanum atom was suggested to be the origin of the observed complex photoelectron peak structures [26–28] and later calculations based on the model developed by Gunnarson and Schönhammer corroborated this assumption [29–31]. The structure of the X-ray photoelectron (XP) spectra results from mixing of the final states with and without charge transfer and with the presence of bonding and antibonding
states. The existence of satellite peaks from multiplet splitting adds to the complexity of the spectra [32,33].

In this work we used an approach aimed at performing reliable peak fitting of the acquired spectra, with few components restricted by constraints, in order to be able to quantify changes between different lanthanum compounds and relate them to changes in interatomic bonding. We characterised bulk materials, in contrast to thin films on substrates, as the crystal and spectral structures in the latter case can be affected by the substrate material and deposition conditions. Results of density of states (DOS) calculations using density functional theory (DFT) were used for the characterisation of the components in the XP valence band spectra and for determining the position of the La 4f orbital above the Fermi level. This is significant in interpreting charge transfer effects from the ligand towards La atoms and the satellite formation in XP spectra of La compounds [29–31].

2. Experimental

2.1. Materials

The base material for the samples used in this work was commercially available lanthanum oxide powder (Alfa Aesar, 99.99% pure). As mentioned above, lanthanum oxide La2O3 is known to spontaneously react with humidity in air to form lanthanum hydroxide La(OH)3, not only on the surface but also in bulk [21,22]. Untreated powder therefore consists of hydroxide and this compound was characterised without further treatment in the present study. In order to form lanthanum oxide La2O3 the powder was heated to 1000 °C for 5 h in a flow of dry nitrogen at atmospheric pressure. This treatment ensures full dehydration of the material, based on results from decomposition studies [21,22]. The treatment was performed in a thermo-chemical reaction chamber attached to the XPS instrument and the sample was transferred to the spectrometer analysis chamber without further exposure to ambient atmosphere, so that rehydration of the sample was avoided. No change in O 1s peak was observed in the course of the characterisation of the La2O3 sample, confirming the absence of reactions during the analysis time.

The samples were characterised in powder form as it is difficult to produce compact bulk samples of these compounds with surfaces that are smooth on an atomic scale. Lanthanum hydroxide cannot be sintered to produce dense pellets since the required high temperatures would cause dehydration of La(OH)3. On the other hand, dense pellets of lanthanum oxide can be produced, but the high reactivity of this compound will cause a rapid roughening of the surface due to the formation of hydroxides and/or carbonates in addition to changing the surface chemistry. Producing dense La2O3 pellets for XPS characterisation will therefore not improve much the sample surface quality compared to powder samples.

Sample powders were filled in a quartz glass powder holder stub. The powders were pressed under vacuum before the analysis using a polished sapphire platelet. This was done in the same operation as the deposition of gold reference nanoparticles (see Section 2.3).

2.2. Instrumentation

SEM images of the gold nanoparticles were taken with a FEI Quanta 200 F in high vacuum mode, using an acceleration voltage of 15 kV.

XPS characterisation was performed on a Kratos Axis Ultra instrument using monochromatic Al Kα (10 mA, 15 kV) and achromatic Mg Kα X-ray radiation (5 mA, 15 kV). The analyser pass energy was set to 20 eV, giving a resolution of 0.53 eV as determined by the full width at half maximum of Ag 3d5/2 using monochromatic Al Kα radiation. Low energy electrons were used to compensate for surface charging. The linearity of the energy scale was calibrated to better than 0.05 eV based on standard binding energy (BE) values for Au 4f7/2, Ag 3d5/2 and Cu 2p3/2 [34]. The base pressure in the analysis chamber was below 6 × 10−7 Pa during analysis.

2.3. Charge referencing

Correct charge referencing of spectra obtained from insulating samples is often a challenge [35,36]. Referencing spectra based on the known BE of one of the components of the sample, a so called internal standard, allows for the most accurate referencing when applicable [37]. This method can, however, only be employed if the constituent used for referencing is in a known chemical state and that its BE shows only negligible energy shifts when the environment is changed; this is clearly not the case for the elements in the present study. An alternative is the use of an external standard, i.e. an added compound with well established BE that equilibrates its Fermi level with the sample. The use of the C 1s peak from adventitious carbon has been rejected for this work as reaction with the sample can be feared during the heat treatment. The deposition of a thin film of reference material does not grant safe energy referencing since owing to the small required film thickness surface and interface effects can induce noticeable shifts [38].

Deposition of nanoparticles of reference material onto the sample surface has shown to give trustworthy results [39,40]. In the method described in these papers gold reference particles were applied onto the sample from a suspension and the carrier liquid was left to evaporate in room atmosphere. There are, however, limitations in directly applying this method in our study, since the particles cannot be deposited on the sample previous to a heat treatment as they can react with the sample material. Moreover, the above described technique does not allow for deposition under vacuum after a treatment. The method has therefore been modified to be applicable for this work. A suspension of gold reference particles (Sigma–Aldrich #636347, particle size < 100 nm) in deionised water was deposited on a polished sapphire platelet instead of directly onto the sample surface. The water was left to evaporate and only gold particles remained on the surface, as shown in Fig. 1 for gold particles deposited according to the same procedure on a silicon wafer (this substrate was chosen to facilitate imaging at high magnification). The sapphire platelet was then mounted on a handling arm in the entry chamber of the XPS instrument. It was pressed under vacuum (p < 7 × 10−6 Pa) onto the sample and gold particles were transferred by contact to the sample surface just before the XPS characterisation.

![Fig. 1. SEM-image of reference gold nanoparticles on silicon.](Image349x627 to 589x784)
For reference the Au 4f\textsubscript{7/2} peak at 83.96 eV BE was employed [34]. The difference in the electric potential between the gold reference particles and the sample surface can be expected to be below 0.05 eV for particles of 100 nm diameter, based on electric field considerations around spherical particles [36]. Good electric contact between the sample surface and the reference particles deposited according to the described method was also verified on conducting samples, where the maximum energy shifts related to differential charging amounted to 0.05 eV [41]. None the less, especially in the case of rough surfaces, an accuracy not better than 0.15–0.2 eV can be expected [37,42].

The utilised charge neutralisation conditions lead to a negatively charged surface. The spectra were shifted during the energy referencing procedure by +4.3 eV BE for La(OH)\textsubscript{3} for acquisitions with both X-ray sources, and for La\textsubscript{2}O\textsubscript{3} by +4.9 eV BE and +4.7 eV BE for acquisitions with monochromatic Al K\alpha and Mg K\alpha, respectively. These amounts were as expected slightly below the energy of the compensating electrons, 4.5V for La(OH)\textsubscript{3} and 5V for La\textsubscript{2}O\textsubscript{3}.

2.4. Data treatment

XPS spectra were treated using the CasaXPS software version 2.3.12 [43].

2.4.1. Quantification

Quantification was performed based on the La 4d, O 1s and C 1s peak areas after a Shirley type background subtraction, before peak fitting with individual components. The limits for the background were set so as to include the whole peak region, excluding plasmon peaks; in the case of La 4d, the high BE limit was set at the lowest point between the photoelectron and the plasmon peaks. Instrument manufacturer’s sensitivity factors were employed.

2.4.2. Lanthanum peak deconvolution

Peak fitting of complex spectral structures can often be achieved in different ways. The obtained results will, therefore, strongly depend on the chosen constrains applied in the deconvolution process. The employed method for the deconvolution of the lanthanum peaks is inspired by the approach utilised by Mullica et al. for the La 3d peaks [44]. The spectrum of each core level was deconvoluted into three peaks: One main peak corresponding to the final state without charge transfer, also denoted c4\textsuperscript{th} (c indicates the presence of a core hole, 4\textsuperscript{th} the absence of electrons in the 4f orbital), and two satellite peaks for the bonding and antibonding component of the final state with charge transfer, denoted c4\textsuperscript{L} and L to mark the transfer of an electron from the ligand atom L to the 4f orbital. We disregard hybridisation between both final states as well as multiplet splitting in order to reduce the amount of peak fitting variables.

Several constrains were applied to the peak fitting parameters during analysis of the different spectral components:

1. The area ratio of peak pairs resulting from the spin–orbit coupling was fixed to the value expected from the ratio of their degeneracy for all peaks (main peaks, satellites and plasmons) [45].
2. The full width at half maximum (FWHM) was identical for both spin–orbit coupling components of all peaks (main peaks, satellites and plasmons).
3. The energy separation of each charge transfer satellite from the related main peak was kept constant for both components of the spin–orbit coupling as the interaction energy with the valence orbitals is not expected to be strongly dependent on the spin orbit interaction.
4. The bonding and antibonding components of the shake-up satellite were fixed to the same area.
5. The energy separation between the photoelectron peak and the plasmon loss structure was kept constant for each sample as the plasmon energy is material dependent and therefore independent of the energy of the emitted photoelectron [45].

6. The area ratio between a component and the related plasmon was kept constant for all components originating from the same orbital.

Peak fitting was done for all photoelectron peaks using Voigt functions after a Shirley type background subtraction. The La 4p\textsubscript{1/2} peak was not considered as this peak suffers important broadening from a giant Coster–Kronig fluctuation [46], neither were the broad La 3p and 4s peaks. The position of La M\textsubscript{4.5}N\textsubscript{4.5} peak maximum was determined by fitting a parabolic curve in a region of ±2 eV around the peak maximum obtained with Mg K\alpha radiation, after a Shirley type background subtraction.

2.4.3. Subtraction of La MNN peaks from La 3d peaks

Monochromatic Al K\alpha radiation is nowadays the most commonly used excitation source for XPS. With Al K\alpha excitation, the strongest lanthanum peaks, La 3d, overlap with the most intense lanthanum Auger peaks, La M\textsubscript{4.5}N\textsubscript{4.5}N\textsubscript{4.5} (hereafter shortened to La MNN). The intensity of this overlap has to be assessed and preferably the La MNN peaks should be subtracted before a throughout characterisation of the components of the La 3d photoelectron peaks is carried out. The Auger peaks can be obtained independently without loss in resolution by using e.g. Mg K\alpha radiation and keeping at the same time the analyser settings identical to the conditions used for the acquisitions with monochromatic Al K\alpha radiation. This is due to the fact that the kinetic energy (KE) and the shape of the Auger peaks are independent of the employed X-ray source as long as the radiation energy is sufficient for the ionisation of the innermost shell of a transition [47]. However, in order to be able to subtract the Auger peak contribution, the relative intensities of the Auger and the photoelectron peaks have to be obtained. This was done according to the method described in Appendix of this article.

The inelastic mean free path values (IMFP) necessary in the subtraction method were obtained using the TPP-2M formula developed by Tanuma et al. [48]. IMFP values were calculated at two energies, at 635 eV KE for the Auger electrons, independently of the X-ray source, and the 3d electrons emitted with Al K\alpha radiation and at 402 eV KE for the 3d electrons emitted with Mg K\alpha radiation. The necessary material parameters for the calculations are given in Table 1. Literature values for the band gap of La\textsubscript{2}O\textsubscript{3} vary from 5.4 eV [49] to 6 eV [6] and 6.4 eV [50]; a value of 5.5 eV has been chosen, by taking the average of the values reported by Prokofiev et al. [49]. No band gap values are available for La(OH)\textsubscript{3}. The band structures obtained from DFT calculations indicate similar band gaps for both materials (see Section 3.3) and the same value as for La\textsubscript{2}O\textsubscript{3} has been used in this work. Variations in the band gap value do not affect much the IMFP ratio used in the formula, even an error of 1.5 eV leads for example to a difference of less than 0.1% in the ratio of the IMFPs of La 3d and La MNN electrons obtained using Mg K\alpha radiation. The uncertainty in the precise band gap energies for La\textsubscript{2}O\textsubscript{3} and for La(OH)\textsubscript{3} has thus no significant effect on the calculations.

The acquired spectrum, i.e. the sum of the contributions from the Auger electrons and photoelectrons, is shown for both compounds in Fig. 2 together with the Auger and photoelectron peaks obtained by the spectra processing method described in Appendix. The graphs reveal an important overlap between the La MNN Auger electron peaks and the La 3d\textsubscript{5/2} photoelectron peaks in both compounds. They also show that there is only a limited interference between the MNN and 3d\textsubscript{5/2} peaks for La(OH)\textsubscript{3}. These peaks do, however, overlap partially in La\textsubscript{2}O\textsubscript{3} and will for example affect
quantification when a background limit is set on the shoulder between the spin-orbit components of the photoelectron peaks.

2.5. DFT calculations

Density functional theory (DFT) [54,55] was utilised to calculate the total and local density of states for lanthanum hydroxide and oxide through the Vienna ab initio simulation package (VASP) code [56,57]. We used soft potentials [58] with the valance electronic configuration of 5s² 5p⁶ 6s² 5d⁷ for lanthanum, 2s² 2p⁴ for oxygen and 1s¹ for hydrogen. The core electrons were described by the PAW method [58,59] which has the advantage of exactly defining the full potential while keeping the efficiency of the pseudopotential method. All calculations were based on the generalised gradient approximation of Perdew et al. (GGA–PBE) [60,61]. The cut-off energy of the plane wave expansion was set to the default value of 400 eV. The density of k-points required for a numerical precision within 1 meV of the total energy was 0.2 Å⁻¹; this was employed for both oxide and hydroxide calculations. The ionic positions and lattice constants were optimised until all forces on the unconstrained atoms were less than 0.05 eV Å⁻¹. Assessed crystal structures of La₂O₃ [62] and La(OH)₃ [53] were used as starting points for the relaxations. To project the DOS onto atomic sites, we used covalent radii of 1.69, 0.73 and 0.37 Å as Wigner-Seitz radii for La, O and H, respectively [63]. In order to access sufficiently detailed structure of the energy states configuration to interpret the valence bands splits, we performed noncollinear calculations to consider spin-orbit (SO) interaction in DOS.

When comparing with the XPS spectra, the obtained DOS plots were broadened using a Gaussian function with a standard deviation of 0.8 eV, corresponding to a FWHM of 1.88 eV, and multiplied by the respective orbitals photoionisation cross sections according to the values tabulated by Yeh and Landau [64].

3. Results

3.1. Quantification

Quantification results are shown in Table 2 together with expected values from the nominal stoichiometry. Measurements including C 1s indicate a carbon content below 8% in both samples. Assuming a uniform contamination film on the surface, this value corresponds to a film thickness of less than 0.2 nm [65]. O 1s has a lower kinetic energy than La 4d, the presence of this contamination layer will thus affect mostly the oxygen peak intensity and cause a slight underestimate of the oxygen content compared to lanthanum. However, the resulting relative error in composition will be of the order of only 1% [65]. The quantification is based on the total peak area, not on individual fitted components. The obtained oxygen content will therefore not only be related to the lanthanum compounds, but also, for a small part, to oxygen bonded to organic contaminants. This concerns especially the lanthanum oxide sample as both the O 1s and C 1s spectra indicate the presence of oxygen containing organic compounds (see Section 4).

The quantification results match, for both compounds, the nominal composition within the uncertainty of the measurement. The oxygen content is at the lower limit of the uncertainty range with respect to the nominal composition of the lanthanum hydroxide sample and could indicate a slight deficiency of oxygen in this sample. Partial dehydration of the sample in the analysis chamber might have occurred due to high vacuum and X-ray irradiation. For the lanthanum oxide sample the uncorrected results match precisely the nominal composition. The oxygen content is slightly reduced (58% O, 42% La) when the presence of oxygen from organic matter is taken into account and subtracted from the oxygen peak. This indicates that only limited amounts of lanthanum hydroxide La(OH)₃ or lanthanum oxocarbonate La₂O₂(CO₃) can be present, since these compounds have a much higher relative content of oxygen atoms.

3.2. Spectral features

The obtained XP-spectra for La and O are shown in Figs. 3–7. The plasmon peaks resulting from the components with the same quantum number are summed in the figures to improve the clarity of the illustrations. The peak positions obtained after peak fitting

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
</table>
| Results from quantification of XPS spectra, in atomic percent. Quantification from XPS spectra is based on La 4d and O 1s peak areas. Uncertainty: ±3%.
<table>
<thead>
<tr>
<th>Compound</th>
<th>La(OH)₃</th>
<th>La₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>La</td>
<td>O</td>
</tr>
<tr>
<td>From XPS spectra</td>
<td>28</td>
<td>72</td>
</tr>
<tr>
<td>From chemical formula</td>
<td>25</td>
<td>75</td>
</tr>
</tbody>
</table>
Fig. 3. La 3d region after subtraction of La MNN peaks, for lanthanum hydroxide La(OH)$_3$ (top) and lanthanum oxide La$_2$O$_3$ (bottom), with the peak fitting components. The peaks without and with charge transfer from the ligand in the final state are labelled $c_{f0}$ and $c_{f1L}$, respectively.

Fig. 4. La 4p region for lanthanum hydroxide La(OH)$_3$ (left) and lanthanum oxide La$_2$O$_3$ (right) with the peak fitting components for the 4p$_{3/2}$ peak. The peaks without and with charge transfer from the ligand in the final state are labelled $c_{f0}$ and $c_{f1L}$, respectively.

are listed in Table 3, the main peak to satellite, the bonding to anti-bonding satellite separations and the relative position of the plasmon peaks in Table 4, and the relative satellite intensities in Table 5.

All characterised La core levels showed satellites. We also observe a weak satellite for La 5s (see Fig. 7), contrary to previous reports in the literature [66,67]. The satellite intensity is stronger and its separation from the main peak is smaller in the oxide

Fig. 5. La 4d region for lanthanum hydroxide La(OH)$_3$ (top) and lanthanum oxide La$_2$O$_3$ (bottom) with the peak fitting components. The peaks without and with charge transfer from the ligand in the final state are labelled $c_{f0}$ and $c_{f1L}$, respectively.
compared to the hydroxide in all characterised orbitals. The satellite intensity in each compound increases with increasing binding energy of the orbital, with the exception of La 4p where the satellite intensity is slightly lower than in La 4d.

The oxygen 1s peak does show more than one component in both materials (Fig. 6). Adequate peak fitting could be achieved with two components in the hydroxide sample, with one clearly dominant main peak. Satisfactory deconvolution of the O 1s spectrum of lanthanum oxide required three components, with one well defined peak on the low BE side of the spectrum and two components in a broad shoulder on the high BE side.

Table 3

<table>
<thead>
<tr>
<th>Component</th>
<th>La(OH)$_3$</th>
<th>La$_2$O$_3$</th>
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<tbody>
<tr>
<td>La 3d$_{x^2-y^2}$ 4f$^5$</td>
<td>851.9</td>
<td>851.7</td>
</tr>
<tr>
<td>La 3d$_{3z^2}$ 4f$^5$</td>
<td>835.1</td>
<td>834.9</td>
</tr>
<tr>
<td>La 4p$_{1/2}$ 4f$^5$</td>
<td>196.3</td>
<td>196.1</td>
</tr>
<tr>
<td>La 4d$_{x^2-y^2}$ 4f$^2$</td>
<td>106.0</td>
<td>105.8</td>
</tr>
<tr>
<td>La 4d$_{3z^2}$ 4f$^2$</td>
<td>102.8</td>
<td>102.6</td>
</tr>
<tr>
<td>La 5s 4f$^5$</td>
<td>35.5</td>
<td>35.9</td>
</tr>
<tr>
<td>La 5p$_{1/2}$</td>
<td>20.0</td>
<td>20.3</td>
</tr>
<tr>
<td>La 5p$_{3/2}$</td>
<td>17.7</td>
<td>17.9</td>
</tr>
<tr>
<td>La $\Delta$4N$<em>{1/2}$N$</em>{5/2}$</td>
<td>622.4</td>
<td>623.1</td>
</tr>
<tr>
<td>O 1s</td>
<td>531.4$^a$</td>
<td>530.5$^a$</td>
</tr>
<tr>
<td>O 2s</td>
<td>529.2$^b$</td>
<td>532.4$^b$</td>
</tr>
<tr>
<td>Valence band 2</td>
<td>9.5</td>
<td>6.3</td>
</tr>
<tr>
<td>Valence band 1</td>
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<td>4.7</td>
</tr>
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</table>

$^a$ Strongest component.
$^b$ Second strongest component.

**Fig. 6.** O 1s region for lanthanum hydroxide La(OH)$_3$ (left) and lanthanum oxide La$_2$O$_3$ (right) with the peak fitting components. See text in the discussion section for the attribution of the different oxygen chemical states.

**Fig. 7.** Valence band region for lanthanum hydroxide La(OH)$_3$ (top) and lanthanum oxide La$_2$O$_3$ (bottom) with the fitted components. Shirley type background subtracted. The peaks without and with charge transfer from the ligand in the final state are labelled 4f$^0$ and 4f$^1_L$, respectively.

Table 4

Relative positions of the La satellite peaks and the plasmon peak, in eV (uncertainty ±0.2 eV).

<table>
<thead>
<tr>
<th>Component:</th>
<th>La(OH)$_3$</th>
<th>La$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La 3d 4f$^0$ to 4f$^1_L$ bonding</td>
<td>3.9</td>
<td>4.9</td>
</tr>
<tr>
<td>La 3d 4f$^0$ to antibonding</td>
<td>2.0</td>
<td>3.7</td>
</tr>
<tr>
<td>La 4p 4f$^0$ to 4f$^1_L$ bonding</td>
<td>3.9</td>
<td>4.1</td>
</tr>
<tr>
<td>La 4p 4f$^0$ to antibonding</td>
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<td>2.6</td>
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<td>3.5</td>
<td>4.1</td>
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<tr>
<td>La 4d 4f$^0$ to antibonding</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
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<td>3.2</td>
</tr>
<tr>
<td>La 5s 4f$^0$ to antibonding</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Photoelectron peak to plasmon</td>
<td>12.3</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Table 5

Relative intensities of La 4f$^0$ (main peak) and 4f$^1_L$ (satellite) states for the various orbitals (uncertainty ±5%).

<table>
<thead>
<tr>
<th>Component:</th>
<th>La(OH)$_3$</th>
<th>La$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La 3d</td>
<td>43%</td>
<td>57%</td>
</tr>
<tr>
<td>La 4p$_{1/2}$</td>
<td>78%</td>
<td>82%</td>
</tr>
<tr>
<td>La 4d</td>
<td>67%</td>
<td>69%</td>
</tr>
<tr>
<td>La 5s</td>
<td>67%</td>
<td>69%</td>
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<table>
<thead>
<tr>
<th>Component:</th>
<th>La(OH)$_3$</th>
<th>La$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La 3d</td>
<td>43%</td>
<td>57%</td>
</tr>
<tr>
<td>La 4p$_{1/2}$</td>
<td>75%</td>
<td>45%</td>
</tr>
<tr>
<td>La 4d</td>
<td>67%</td>
<td>49%</td>
</tr>
<tr>
<td>La 5s</td>
<td>67%</td>
<td>49%</td>
</tr>
</tbody>
</table>
The valence band region is characterised by several features, including the band structure near the Fermi level (sometimes also called "outer valence band"); the La 5p and 5s peaks as well as the O 2s peak. Adequate peak fitting required two components for the band structure, two for La 5p, three for La 5s and one component for O 2s. A second O 2s component was added for the lanthanum oxide spectrum to reflect the structure of the O 1s region in this compound. The separation and intensity ratio between these two O 2s components was set to the same values as for the La₃O₅ related peaks in the O 1s core level. A comparison of the valence band of both compounds shows that an additional peak is present in the hydroxide compared to the oxide in the energy range between 8 and 11 eV BE (Fig. 7). It can furthermore be noted that the lanthanum related peaks are broader in the oxide than in the hydroxide, the FWHM of the fitted La 5p½ peak is for example 2.7 eV in La₂O₃ but only 1.7 eV in La(OH)₃. Their relative peak positions are also shifted compared to the core orbitals: While the core level orbitals are consistently – but within the uncertainty limits – lower by 0.2 eV BE in lanthanum oxide compared to lanthanum hydroxide, the shallow La 5s and La 5p orbitals show an opposite shift, with their peak position being higher by 0.2–0.4 eV BE in the oxide compared to the hydroxide.

3.3. DFT calculations

The results from the DOS calculations of the valence and conduction bands of lanthanum oxide and hydroxide are shown in Fig. 8. For La(OH)₃ the valence band is composed of two regions, both mostly O-p character. The low BE part has a weak contribution from La orbitals while the high BE part shows contributions from O-s and H-s orbitals and, much weaker, from La orbitals. The conduction band is mainly of La-f character with weak contributions from La-d and O-p orbitals. The band gap is 3.69 eV and the centre of mass of the La 4f level and the valence band is separated by 6.16 eV. For La₂O₃ the valence band is likewise mostly of O-p character, with contributions from La orbitals. The O-p character is weaker and the contribution from lanthanum stronger for this compound than for the hydroxide, indicative of a less ionic character of the O–La bond in the oxide. The conduction band is mainly of La-f character with some contribution from La-d. The band gap is 3.87 eV, slightly higher than in the hydroxide, while the centre of mass of the La 4f level and the valence band are separated by 6.05 eV, a slightly lower separation than in the hydroxide. It has to be noted that the absolute value of band gaps are underestimated and the related parameters are correspondingly shifted in DFT based calculations [68]. The differences between the compounds can still be used in subsequent discussions.

The difference in bond ionicity for the two compounds affects also the DOS of the shallow O 2s and La 5p orbitals. While the DOS for these orbitals are concentrated in narrow peaks in the ionic lanthanum hydroxide, they are spread into band-like structures in the more covalent lanthanum oxide.

The comparison of the valence band region obtained from DFT and XPS shows an overall good agreement between the calculations and the experiment (Fig. 9). The calculations do reproduce well the difference observed in the valence band between the two compounds, i.e. the presence of a doublet for lanthanum hydroxide and a singlet for lanthanum oxide in the energy range 5–10 eV, as well as the difference in width of the La 5p peaks between the two compounds. The DOS calculations underestimate the separation between the valence band and the shallow, La 5p and O 2s orbitals and, for lanthanum hydroxide, the separation between the latter orbitals.

4. Discussion

4.1. Charge referencing

In this work we applied gold nanoparticles for charge referencing right before the acquisition of the XP spectra (see Section 2 above). In this way we make sure that the procedure is identical for untreated samples and samples treated in situ and ensures consistent charge referencing. The surface potential of the samples during the measurements, and hence the magnitude of the peak shift applied during the energy referencing procedure, was similar but not identical for acquisitions on the same sample with different X-ray sources. Differences in surface charging are expected between monochromatic Al Kα and achromatic Mg Kα. The X-ray flux will be lower for a monochromatic source than for an achromatic source operated at the same power due to the losses in the monochromator. On the other hand, secondary electrons are generated from the window separating the achromatic source from the sample, and these secondary electrons will participate to the charge compensation in addition to the electrons from the charge compensation source. The effective potential at the sample surface results from the equilibration of all electron fluxes [36], acquisitions carried out with different X-ray sources will, therefore, not necessary lead to exactly the same amount of surface charging.

A comparison of the Au 4f½/2 and C 1s spectra shows clearly that the adventitious carbon present on the samples has undergone a change in chemistry during heat treatment (Fig. 10). The strongest component of the C 1s spectrum of the lanthanum hydroxide sample lies at 285.1 ± 0.2 eV BE, typical for carbon bonded to carbon or hydrogen [69]. The C 1s peak of the lanthanum oxide sample is broader with its maximum positioned in the range 285.6–287.8 eV BE at, at energies typical for carbon with a single or double bond with oxygen [69]. These results indicate that the carbon contamination, already present initially on the sample, is oxidised during the heat treatment. Referencing with adventitious carbon can thus not be used for situ treated lanthanum oxide samples.

The presence of a carbon peak from a fluorinated organic contamination can be noted in the C 1s spectrum for both samples (peak C in Fig. 10). This peak appeared on the samples together with a fluorine peak after the sample being in the analysis chamber for several hours. The measured fluorine to carbon ratio was approximately 1.1 for La(OH)₃ and 1.3 for La₂O₃, based on peak areas from the survey spectra and corrected, for carbon, to only account for the amount of carbon bonded to fluorine as it was determined in the high resolution spectrum. This ratio was lower than what is expected (2–to-1 if C-F₂ bonds dominate), but the precision in the results suffer from the low intensity of the peaks and the low resolution from the survey scan. The BE of this carbon peak remains constant for both samples, an additional confirmation of the consistency of the employed charge referencing method.

4.2. XP spectra

4.2.1. Lanthanum peaks

The area ratio between the 3d₅/₂ and 3d₇/₂ peaks is theoretically 1.5, considering the degeneracy ratio, and a satisfactory peak fitting was possible using this value. A ratio of approximately 1.4 has, however, been reported previously for lanthanum hydroxide and oxide [66,70]. Al Kα radiation was used in these studies, but the presence of the La MNN peaks was not taken into consideration. We attribute therefore the discrepancy between these reported values from the theoretical ones and our own results to the fact that previous studies did not take into account the presence of the La MNN Auger peaks.

The satellite to main peak intensity ratio is highest for La 3d for both analysed compounds, much higher than for the lower BE peaks
Fig. 8. Density of states around the Fermi level obtained by DFT calculations for lanthanum hydroxide La(OH)$_3$ (left) and lanthanum oxide La$_2$O$_3$ (right). The oxygen and hydrogen DOS are shown in the first row and lanthanum DOS in the second row, the total DOS is shown as shaded area. The energy of the highest occupied level is set to zero. For clarity only orbitals with a maximum DOS higher than 1 state/eV/unit formula are shown.

Fig. 9. XP spectra of the valence band and density of states obtained by DFT calculations, both as calculated and broadened with a Gaussian function, for lanthanum hydroxide La(OH)$_3$ (left) and lanthanum oxide La$_2$O$_3$ (right). The calculated DOS are corrected for the differences in the orbitals’ sensitivity factors and the position along the energy scale is shifted to fit the experimental results for the lanthanum peaks.

(Table 5). This has previously been attributed to a weaker final state interaction between the core hole and the 4f orbital compared to the 3d orbital and, as a consequence, less hybridisation between the La 4f orbital with the valence band [29,33]. The slightly higher satellite intensity obtained for La 4d compared to La 4p can result from the uncertainty in the peak fitting, especially in the case of La 4d where many components overlap. It could also be related to differences in the multiplet splitting in the 4p and 4d orbitals, a multiplet splitting that has not been taken into account in this work.

When comparing the spectra from La(OH)$_3$ and La$_2$O$_3$ the same tendencies are observed for the satellite positions and intensities for all core electron peaks. The peak separation between bonding to antibonding satellites and the relative intensity of the satellites compared to the main peak increase from the hydroxide to the oxide. This can be related to a stronger hybridisation between the

Fig. 10. Au 4f$_{7/2}$ (left) and C 1s (right) peaks for La(OH)$_3$ and La$_2$O$_3$ after charge referencing on Au 4f$_{7/2}$. In the C 1s spectrum peak A is attributed to C–C bonds, peak B to C–O and C=O bonds and peak C to C–F$_2$ bonds [69].
4f orbital and the valence band in the final state for La$_2$O$_3$, as such a hybridisation will increase both the satellite intensity and the separation between the bonding and antibonding states of the satellite [29]. These results can be interpreted in the sense of a smaller separation in energy between the valence band and the 4f orbital and a stronger hybridisation in the initial state for the oxide compared to the hydroxide [29], in agreement with the results from our DFT calculations. This in turn would correspond to a larger covalency of the La–O bonds in La$_2$O$_3$ compared to La(OH)$_3$, again in agreement with our results from DFT calculations. This is also expected from the respective electronegativities of lanthanum and hydrogen: The presence of O–H bonds in the hydroxide, with hydrogen being more electronegative than lanthanum, will induce an increased ionicity of the La–OH bonds compared to the oxide where only La–O bonds are present [71]. The electronic polarisability of the ligand atom is another parameter that can influence the hybridisation in the final state, as a higher polarisability will favour a stronger interaction in the final state between the ligand valence band and the lanthanum 4f orbital. As known, the intensity of this polarisability can be evaluated by measuring the Auger parameter $\alpha$ [72]. The measured Auger parameter value is higher in the case of lanthanum oxide than lanthanum hydroxide (1474.8 eV versus 1474.3 eV, based on La 3d$_{3/2}$ 4p$^0$ and M$_{4.5}$N$_{4.5}$N$_{4.5}$ values, Table 3). Although the difference in $\alpha$ is near the uncertainty limits, the observed trend is in agreement with the difference in hybridisation deduced from the lanthanum spectra and DFT calculations.

4.2.2. Oxygen peaks

A doublet is present in the O 1s spectrum of lanthanum hydroxide (Fig. 6). The most intense peak is located at 531.4 eV BE, which is close to literature values reported for this compound [24,25,66]. The second, weaker peak at 529.2 eV BE can be attributed to oxidic bonds, as opposed to hydroxide bonds. The presence of residual La$_2$O$_3$ in the sample is unlikely as the spontaneous hydration process is rapid and not only restricted to the surface [21,22]. We attribute this peak to oxygen atoms after partial dehydration of La(OH)$_3$ in the analysis chamber of the instrument caused by the combined effect of high vacuum and X-ray irradiation. A partial dehydration of the compound is in agreement with the quantification results shown in Table 2 which indicate a small depletion of oxygen compared to the nominal composition. This interpretation is also strengthened by a slight increase of the low BE peak, accompanied by a corresponding decrease of the main peak, between the two independent sweeps of the acquisition. As this dehydration takes place at room temperature recrystallisation into the stable oxide crystal structure will be hindered. The binding energy of these oxygen atoms originating from this process is thus expected to differ from the value for oxygen in La$_2$O$_3$. Angle resolved XPS (ARXPS), with its ability to discriminate between surface and bulk signal, would give useful contribution to the understanding of the sample surface composition. However, the inherent surface roughness of the powder samples inhibits meaningful ARXPS measurements [73].

Two peaks are also present in the O 1s spectrum of lanthanum oxide (Fig. 6). The strongest peak at 530.5 eV BE is inside the notably wide range of energies reported for oxygen in lanthanum oxide (following BE have for example been reported: 528.4–532.8 eV [74], 528.4 eV [75], 529.8 eV [24], 529.9 eV [76], 530.5 eV [77]). The second peak at higher binding energy has been reported before and been attributed to either adsorbed water [75,76], hydroxyl groups [24] or O$^-$ surface atoms [24]. Quantification does not indicate any large deviation from the expected stoichiometry in our measurements, thus the presence of a significant amount of oxygen rich surface species can be excluded. The absence of the spectral features related to OH-bonds in the valence band spectrum for this compound excludes also the presence of adsorbed water or hydroxyl groups on the surface of the sample (see below the discussion of the valence band structure). Structural effects are therefore thought to be the origin for the doublet. The stable form of La$_2$O$_3$ has a hexagonal structure [78] in which all the lanthanum atoms have equivalent positions with a seven-fold coordination to oxygen. Oxygen atoms are, however, distributed on two different sites. Two thirds are located at a four-coordinated position O1 with the La–O bond lengths being between 2.36 and 2.42 Å and one third are at a six-coordinated position O2 with La–O bond lengths equal to 2.72 Å. The differences in coordination and bond length between O1 and O2 can induce a shift in binding energy measured by XPS due to both initial and final state effects. Bond valence calculations performed on La$_2$O$_3$ indicate a significantly higher negative charge on O1 than O2 (difference in bond valence sums of 0.89, O1 having an excess of electrons and O2 being electron deficient relative to the nominal -2 oxidation state) [79], and thus, considering initial state effects, this would lead to a lower BE for O1 than O2 [72,80].

Extra-atomic relaxation will also differ between O1 and O2 due to the difference in coordination and bond length [81]. We calculated the extra-atomic relaxation energy $R^\alpha$ for each oxygen site by applying the formula presented in reference [72] for structures where all the ligands are equivalent:

$$R^\alpha = \frac{7.2n\alpha}{R^4 + R\Delta\alpha}$$

(1)

where $n$ is the number of ligands, $\alpha$ the electronic polarisability of the ligand (lanthanum in this case with $\alpha = 1.05\,\AA^3$ [82]), R the bond length and $D$ a geometrical factor equal to 1.15 for a tetragonal arrangement of the ligands and 2.37 for an octahedral arrangement [81]. The obtained relaxation energies are 0.87 eV for O1 and 0.73 eV for O2. The difference in the extra-atomic relaxation energy will induce a slightly lower BE for O1 than O2 from a final state point of view.

Both initial and final state effects indicate thus a lower BE for O1 than O2. Peak fitting the obtained spectrum using two components, with an O1:O2 peak area ratio of 2:1 did not lead to satisfactory results. The addition of a third, low intensity peak O3, to account for C–O bonds related to the detected oxidised adventitious carbon (see Fig. 10), enabled adequate fitting of the experimental spectrum (Fig. 6). The O3 peak intensity corresponds to an oxygen to carbon ratio of 1.2, taking into account both carbon peaks that we relate to oxygen bonds.

It has to be noted that the peak positions of O2 and O3 are uncertain due to their large overlap, adequate peak fittings can be achieved with different combinations of peak positions and intensities. The presented decoupling is based on a minimisation of both the energy separation of O1 and O2 and of the O3 peak intensity.

4.2.3. Valence band

Differences in peak position and width are observed between La(OH)$_3$ and La$_2$O$_3$ in the valence band region. The valence band itself is for both compounds mostly of oxygen 2p character. However, it shows a clear doublet in the hydroxide while it is concentrated in a single band in the oxide. The presence of density of states related to lanthanum in the low BE component of the valence band, the component present in both materials, permits to relate this part of the valence band to the O–La bonds. The higher BE part of the valence band, only present in lanthanum hydroxide, contains contributions from O s and H s orbitals and can thus be related to the O–H bond. These assignments are in agreement with previous attributions of the low BE components to O 2p$\pi$ bonds, the high BE components to O 2p$\sigma$ bonds [66]. The absence of the high BE component related to OH in the XP spectrum for La$_2$O$_3$ confirms once more the absence of OH-groups on the surface of this sample.
The difference in peak width of the shallow La 5s and La 5p orbitals of La$_2$O$_3$ as compared to La(OH)$_3$ can be related to the participation of these orbitals in the covalent bonding in the oxide. Covalent interaction between these lanthanum orbitals with oxygen orbitals is expected to induce the formation of band like structures causing a broadening of the peaks in the XP spectrum. This is clearly shown in the results from the DFT based calculations.

5. Conclusions

We have described a technique for depositing gold nanoparticles in vacuum on in situ treated samples for charge referencing in XPS analysis. This enabled reliable charge referencing of lanthanum oxide formed after in situ heating of lanthanum hydroxide. The use of the adventitious carbon would lead to erroneous results as the carbon undergoes oxidation during sample treatment.

We also developed a method for subtraction of the La MNN peaks present in the energy region of La 3d peaks when Al Kα is employed, based on acquisitions with both achromatic Mg Kα and monochromatic Al Kα X-ray sources. It is thus possible to take advantage of the higher spectral resolution achievable with monochromatic Al Kα compared to achromatic X-ray sources, without interference with lanthanum Auger peaks. The characterised lanthanum photoelectron peaks, 3d, 4p and 4d, could be satisfactorily deconvoluted using a combination of three types of components, with strong constraints on their intensities and positions, for each level after the spin-orbit splitting has been taken into account: one main peak related to the photoemission without charge transfer to the La 4f orbital, two satellite peaks associated to the final state with charge transfer from the ligand valence band to La 4f and a plasmon for each of these three peaks.

The obtained photoelectron spectra of La(OH)$_3$ and La$_2$O$_3$ show notable differences. The satellite intensity relative to the main peak is lower in the hydroxide compared to the oxide. This is in agreement with its higher ionicity and larger separation between the valence band and La 4f DOS as obtained from the DFT calculations. The valence band structure of La(OH)$_3$ shows in the energy region 8–11 eV BE a peak associated to the O–H bond, a peak which is absent from the XP spectrum of La$_2$O$_3$. The O 1s peaks of the two compounds differ also: while it is practically a singlet for the hydroxide it shows a notable second component on the high BE side for the oxide. We relate the two components of the O 1s peak in lanthanum oxide to the two distinct positions of oxygen in the crystal structure of this compound, the four-coordinated atoms having a lower binding energy than the six-coordinated ones due to both initial and final state effects.

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Appendix. Procedure for subtraction of La MNN from La 3d peaks

The signal strength $I_i$ of a photoelectron peak of energy $e_i$ is related to the flux of the incoming X-rays $I_0$, the volume concentration of the parent atom $\eta_i$, the photoexcitation probability or cross section $\sigma_i$, the inelastic mean free path (IMFP) for the considered photoelectrons in the material, $\lambda$, and the fraction of the emitted electrons of a given energy detected by the detector-analysers combination, $D$, also called transmission function. The relation is thus [83]:

$$ I_i = I_0 \eta_i \sigma_i (e_i) D(e_i) $$  \hspace{1cm} (2)

The same equation is also valid for Auger peaks if the probability $P_i$ of the Auger decay after initial ionisation is added:

$$ I_i = I_0 \eta_i \sigma_i P_i (e_i) D(e_i) $$  \hspace{1cm} (3)

$\sigma_i$ is then the photoexcitation cross section for the electrons in the initial orbital of the considered Auger transition. When setting up an intensity ratio between a photoelectron peak and an Auger peak acquired under the same conditions, both $I_0$ and $\eta_i$ are identical and cancel out. The intensity ratios between the La 3d and La MNN peaks for Al Kα and Mg Kα radiation can thus be written as:

$$ I_{3d, \text{Al} K\alpha} = \frac{\sigma_{3d, \text{Al} K\alpha} \cdot \lambda_{3d, \text{Al} K\alpha} \cdot D_{3d, \text{Al} K\alpha}}{I_{\text{MNN}, \text{Al} K\alpha} \cdot \sigma_{\text{MNN}, \text{Al} K\alpha} \cdot \lambda_{\text{MNN}, \text{Al} K\alpha} \cdot D_{\text{MNN}, \text{Al} K\alpha}} $$  \hspace{1cm} (4)

The subscripts contain here first the photoelectron or Auger electron transition while the X-ray radiation is denoted after the comma. The MNN Auger transitions considered here, M$_{\text{L3}}$N$_{\text{L3}}$N$_{\text{L3}}$, originate from 3d core holes, i.e. the same orbitals as the photoelectron peaks they are compared with. The photoionisation cross sections $\sigma_{3d}$ and $\sigma_{\text{MNN}}$ are thus equal for the same excitation energy. The probability of an Auger decay arising after ionisation is constant and does not depend on the source of the ionisation, i.e. $P_{\text{MNN}}$ is identical for Al Kα and Mg Kα radiation. Eq. (4) simplifies thus to:

$$ I_{3d, \text{Al} K\alpha} = \frac{\alpha_{\text{MNN}, \text{Al} K\alpha} / \lambda_{\text{MNN}, \text{Al} K\alpha} / D_{\text{MNN}, \text{Al} K\alpha}}{\alpha_{3d, \text{Al} K\alpha} / \lambda_{3d, \text{Al} K\alpha} / D_{3d, \text{Al} K\alpha}} $$  \hspace{1cm} (5)

In this work we characterised peak intensities by measuring peak areas $A$ after a three-parameter Tougaard background subtraction, and the transmission function was integrated during the calculations. In addition, the kinetic energy of the MNN Auger electrons are similar to the 3d photoelectrons for Al Kα radiation, their respective IMFP values are thus similar. Eq. (5) becomes then:

$$ \frac{A_{3d, \text{Al} K\alpha}}{A_{\text{MNN}, \text{Al} K\alpha}} \equiv \frac{A_{3d, \text{Mg} K\alpha}}{A_{\text{MNN}, \text{Mg} K\alpha}} \cdot \frac{\lambda_{\text{MNN}, \text{Mg} K\alpha}}{\lambda_{3d, \text{Mg} K\alpha}} $$  \hspace{1cm} (6)

Due to the overlap of the 3d, Al Kα and MNN, Al Kα peaks, their individual areas cannot be acquired independently, only their sum $A_{\text{total}, \text{Al} K\alpha} = A_{3d, \text{Al} K\alpha} + A_{\text{MNN}, \text{Al} K\alpha}$. By introducing this value into equation 6 and rearranging the terms it is, however, possible to separate the Auger contribution to the total area:

$$ A_{\text{MNN}, \text{Al} K\alpha} \equiv \frac{A_{\text{total}, \text{Al} K\alpha}}{1 - (A_{3d, \text{Mg} K\alpha} / A_{\text{MNN}, \text{Mg} K\alpha} \cdot \lambda_{\text{MNN}, \text{Mg} K\alpha} / \lambda_{3d, \text{Mg} K\alpha})} $$  \hspace{1cm} (7)

The intensity $I$ of the Auger peak at kinetic energy $x$ obtained from Al Kα radiation excitation is then related to the intensity of the same peak using Mg Kα radiation by:

$$ I_{\text{MNN, Al} K\alpha}(x) = I_{\text{MNN, Mg} K\alpha}(x) \cdot \left( A_{\text{MNN, Al} K\alpha} / A_{\text{MNN, Mg} K\alpha} \right) $$  \hspace{1cm} (8)

and the intensity of the 3d photoelectron peak becomes thus:

$$ I_{3d, \text{Al} K\alpha}(x) = I_{\text{total, Al} K\alpha}(x) - I_{\text{MNN, Al} K\alpha}(x) $$  \hspace{1cm} (9)

This is the La 3d part of the total spectrum obtained with monochromatic Al Kα radiation, and the resolution on these photoelectron
peaks is higher than what can be achieved with achromatic Mg Kα radiation.

The above development is strictly valid only for monochromatic X-ray sources as Auger peaks also appear after ionisation from bremsstrahlung in achromatic X-ray sources, i.e. the relative intensity of the Auger peak is then higher. Comparison between monochromatic and achromatic X-ray radiation indicates a contribution of the order of 15% from bremsstrahlung for Al Kα radiation [84], this amount has therefore been subtracted from $\Delta M_{\text{NN}, \text{Mg Kα}}$ in our calculations.

References


