Surface structure and composition of Pt\textsubscript{50}Rh\textsubscript{50}(110): room temperature analysis of the (1 × 3) missing-row reconstruction

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Abstract

The room temperature structure and composition of the clean Pt\textsubscript{50}Rh\textsubscript{50}(110) surface is investigated by low energy ion scattering (LEIS), scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and grazing incidence X-ray diffraction (GIXRD). While Pt\textsubscript{25}Rh\textsubscript{75}(110) reconstructs with a (1 × 2) missing-row structure, Pt\textsubscript{50}Rh\textsubscript{50}(110) exhibits a (1 × 3) structure in analogy with Pt\textsubscript{80}Fe\textsubscript{20}(110) and Pt\textsubscript{90}Co\textsubscript{10}(110). Three missing rows lead to the formation of (111) facets in which all atomic sites are enriched with platinum. Similarly all sites directly underneath are enriched with Rh leading to oscillation of the Pt concentrations similar to that of (111) surfaces. These composition changes are accompanied by a marked inwards relaxation of the top row (~10%) and large buckling in layers 3–5. Additionally the atomic positions of the facets are shifted laterally towards the valleys formed by the missing rows. Consistent pictures are derived from LEED, GIXRD, STM and LEIS concerning the composition while some discrepancy—similar to that recorded for pure Pt—are found concerning the interlayer distances between LEED and X-rays.

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1. Introduction

Among bimetallic alloys, the PtRh system is of particular importance due to its wide range of industrial applications and more particularly as automotive three-way catalyst. This is why it has motivated fundamental research devoted to its chemical properties and to the detailed characterization of its surfaces. Experimental work has been recently dedicated to Pt\textsubscript{25}Rh\textsubscript{75} with emphasis on the chemical composition and local ordering in the (111) and (100) surfaces [1,2]. Low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) works have shown that the (110) surface reconstructs with a (1 × 2) missing-row structure [1,3] in the fashion of the noble
metal reconstruction and other bimetallic alloys. However, the PtRh system is only partially known and there are still open questions. This is also, in the large series of bimetallic alloys, a special case as this is one of the few alloys for which no ordered phase has been reported.

Among the many parameters that influence the catalytic properties of alloys, the bulk concentration plays a particular role as it allows varying the surface layer composition and the interatomic distances, which drive the surface atomic arrangement. In the case of PtRh, increasing the bulk Pt concentration leads to changes in the reconstruction, from a \((1 \times 2)\) for Pt\(_{25}\)Rh\(_{75}\)(110) to a \((1 \times 3)\) symmetry for Pt\(_{50}\)Rh\(_{50}\)(110).

The surface structure and composition depend on the subtle balance between the various energetic terms whose contributions are also strongly dependent on the chemical nature of the element alloyed to Pt. Indeed, the existence of several periodicities in missing-row reconstructions has already been reported for Pt, Ir and Au(110) but also for at least one Pt–metal bimetallic alloy, Pt\(_{80}\)Fe\(_{20}\)(110) which yields \((1 \times 2)\) or \((1 \times 3)\) missing-row (MR) structures depending on the annealing temperature [4–6]. Additionally, a missing-row reconstruction with \((1 \times 3)\) periodicity has been recently analysed for the Pt\(_{80}\)Co\(_{10}\)(110) [7] surface while the same alloy does not reconstruct for lower bulk Pt content and shows large Co segregation to the top layer [8] as opposed to the massive Pt segregation observed on the denser faces. Similarly Ni rich Pt\(_x\)Ni\(_{1-x}\)(110) alloys keep the bulk fcc structure up to the surface with Ni segregation in the top layer [9–13].

While the surfaces of alloys of Pt with 3d metals (Fe, Co, Ni) have been studied quite extensively in the past, less is known about the surfaces of its alloys with 4d metals and the corresponding reconstructions. It can be postulated that the same basic mechanisms are at the origin of the \((1 \times n)\) MR arrangement for both 3d and 4d metals. Robinson et al., following the works of others have pointed out that the top two layers of Pt(1 1 0)(1\times 3) are prone to significant contraction [14] and that the structure may be stabilized by impurities that locally release the strains. The case of PtRh and more commonly of alloys in which the—smaller radii—3d or 4d metals may play the role of “impurities” in the equilibrium, allows to draw general conclusions as to MR reconstruction and in particular regarding the significantly reduced interatomic spacings.

An additional parameter in the building of the surface structure is the annealing temperature as segregation and hence reconstruction are drastically affected by this parameter. The detailed temperature-dependent behaviour will be reported in a forthcoming paper [9]. In this first part we focus essentially on the room temperature structure. In order to determine the atomic positions and chemical content we have used a series of four probes relying on different physical processes and sensitive to quite different parameters. STM for the local arrangement and morphology, low energy ion scattering (LEIS) which is sensitive to the surface composition, grazing X-rays surface diffraction in order to have a large sensitivity to in-plane parameters and LEED which allows to determine the out-of-plane parameters as well as the composition several layers deep.

2. Experimental details

The LEED experiments were carried out in Grenoble, in a vacuum chamber equipped with hemispherical optics (glass screen and grids) used for quantitative LEED and Auger electron spectroscopy (AES) for control of the sample cleanliness. The X-rays measurements were performed on the French CRG-IF beamline (BM32) at the ESRF where LEED is also available. Finally, the LEIS and STM studies were performed in Vienna, using two separate UHV chambers.

The pressure is in the low \(10^{-10}\) mbar range or below and standard surface preparation equipment (ion gun, heater and Auger spectroscopy) is available in all chambers.

In order to avoid differences due to the samples, the same sample was used in all chambers. Cut from a rod, it was oriented with a miscut smaller than 0.2° after mechanical polishing. The first cycle of cleaning under UHV conditions included a 2 h sputtering, a flash anneal at 1200 °C followed by 3 min at 1100 °C.
The same procedure was then followed in all chambers for the preparation of the crystal: a clean and reproducible surface was obtained by repeated cycles of sputtering (typically \(5 \times 10^{-7}\) and \(10^{-4}\) Torr Ar, 0.5–2 keV, 1.5–10 \(\mu\)A) and annealing at temperatures around 900 °C. As illustrated by the good reproducibility of LEED \(I(V)\) spectra, this temperature was not crucial for the surface structure and composition measured at room temperature provided it was larger than 800 °C.

For the LEED study, whole images were collected, in 1 eV steps from 40 to 360 V, at room temperature, at normal incidence (alignment better than 0.1°), using a video system. The \(I/V\) spectra were then extracted from the images after background subtraction, normalized for a constant incident current and averaged over equivalent spots to reduce the noise and effect of residual misalignments.

The analysis was then performed with 21 non-equivalent beams (7 integer and 14 fractional order beams) up to a maximum of 321 V for a total energy range of \(\Delta E = 3830\) eV.

LEIS experiments were carried out using He\(^+\) ions with 1 keV energy. The mass selected ion beam was defocussed to minimize sputtering effects (intensity 1 nA/mm\(^2\)). The scattered ion energy was analysed at constant resolution with a hemispherical analyser. Data were collected, for the room temperature reconstructed surface, at two scattering angles (\(\Theta = 60^\circ\) and 120°) along two main directions of the crystal (see Fig. 1). For the quantification of the surface composition we used single crystal Pt(111) and Rh(111) standards.

The grazing incidence surface diffraction measurements were performed at 18 keV photon energy, which allows exploring a large portion of the diffraction rods. The experimental set-up consists of an UHV chamber mounted on a \(z\)-axis diffractometer, which is described elsewhere [15]. The diffraction rods were measured at an incidence angle of 1.5°.

After the standard preparation, the room temperature LEED pattern exhibits a \((1 \times 3)\) reconstruction and \(p2\)mm symmetry. This is somewhat different from Pt\(_{25}\)Rh\(_{75}\)(110) for which a \((1 \times 2)\) reconstruction is observed [1,3]. The background is very low and the spots appear rather sharp although slightly elongated in the [001] direction.

As explained below, the surface layers differ markedly from the bulk ones due to segregation and reconstruction but in no case did we detect any trend towards chemical ordering within the surface slab in the manner observed for Pt\(_{80}\)Fe\(_{20}\)(1 1 0)-(1 \(\times\) \(n\)) which reconstructs similarly [4]. Furthermore, PtRH is known for its low trend to order.
chemically, in surface as well as bulk layers. Finally, the average row or facet Rh concentrations derived from diffraction techniques are too low to permit any specific ordered unit cells. As a consequence no attempt was made in the LEED analysis to optimise the in-plane distribution of chemical species: all layers were assumed to contain a random mixture of Pt and Rh sites [16].

3. Model and STM

The conclusion of a missing-row type reconstruction is straightforward and follows from: (1) the striking similarities of the $I/V$ LEED spectra with those of previously investigated similar surfaces—Pt(1 1 0)-(1 × 3) [17], Pt$_{80}$Fe$_{20}$(1 1 0)-(1 × 3) [5] or Pt$_{90}$Co$_{10}$(1 1 0)-(1 × 3) [7]—for which it was demonstrated that two rows out of three in the top layer and one out of three in layer 2 are missing; (2) from STM images (Figs. 2 and 3).

Indeed, large-scale STM images exhibit close-packed rows, which extend over thousands of Å in the [1 1 0] direction and are separated by a distance of about 11.5 Å, i.e. close to three times the lattice parameter (11.58 Å) (Fig. 2). These arguments were judged sufficient to limit the LEED analysis to the structural model schematised in Fig. 1 and to discard definitely any other possibility with fewer missing rows in the top layer or other geometries such as the “saw tooth” or “pairing” models which produce quite unlike $I/V$ spectra and would yield different STM images. A few LEED runs were however performed to investigate the possibility of a complete second layer. The conclusion is not ambiguous: the $R$-factors increase by a factor of ~1.5 with respect to the previous model indicating that a row is actually missing in layer 2. This conclusion is supported by the corrugation observed by STM (~2 Å perpendicular to the rows) and by similar tests with the X-ray data: a model with two missing rows in layer 1 above a complete layer 2 results in twice higher $\chi^2$ values after optimisation of all parameters.

Clearly the morphology is not perfect and, in agreement with the above mentioned elongation of the LEED spots, we do find out that the terraces,
several hundreds or thousands Å long in the [1–10] direction have shorter extension along the [001] axis. Additionally, in the same direction, there is some disorder: a few very narrow areas are covered by (1 × 2) reconstruction and, here and there, some isolated rows protrude over the terraces or rows may be interrupted. Finally, we also observe some domain boundaries on the terraces.

The atomic resolution permits to see that, along the dense rows, some rare vacancies occur, but generally speaking, the outermost rows appear quite homogeneous. Only in some rare images (Fig. 3) do we see a clear contrast between two species. This may be due to chemical contrast (Rh appears brighter as in Ref. [1]) or due to a different environment of the atoms. The number of dark species is 83% in Fig. 3 and 90% in another image, not shown here. By comparison with LEED and LEIS figures (see below), these concentrations allow to clearly identify the bright species as Rh.

4. LEIS

On a macroscopic scale, we determined the top-layer composition of Pt₅₀Rh₅₀(110) by LEIS, in two scattering configurations. In the first one (θ = 60°, α = 30°, φ = 35.2°) the incoming and detected ions were aligned with the [0–11] and [1 0 1] directions, respectively (see Fig. 1). In such conditions, deep atomic layers are geometrically shadowed and blocked by those of the topmost layer. Due to the low survival probability of 1 keV He⁺ ions (few per cent), and due to the low cross-section for double scattering in the top plane, the detected ions come solely from the first layer after single elastic scattering events. In the second scattering geometry, the ion beam is aligned along the [0 0 1] direction (θ = 120°, α = 60°, φ = 0°) so that all atoms of the (1 1 1) facets contribute to the fitted composition.

The quantification of the top-layer composition was done by means of a least-square fit of standard spectra to the alloy spectra. The room temperature analysis of the (1 × 3) structure was part of a variable temperature study, which will be published later on.

In the θ = 60° configuration, the Pt concentration of the top row was found to be C₁ = 92%, and 96% Pt in another series of measurements. This higher value is certainly due to slower cool-down that, via ion-induced and thermal mobility, allows reaching a higher Pt concentration at low T. The facet-averaged concentration obtained in the other incidence condition (θ = 120°) is somewhat lower, C₁ = 87% Pt, compared to 89% derived from the LEED calculations (see below). This means that the top row has a slightly higher Pt content than the rest of the facet that now contributes to the signal.

5. Calculation details: LEED and X-ray diffraction

5.1. LEED

Calculations were performed independently in Grenoble and Vienna using the same data set but different programs [18,19], different phases shifts (both relativistic and spin averaged) and optimisation procedures [20,21].

The random distribution of Pt and Rh sites was accounted for via the average-t-matrix approximation (ATA) [16]. The quality of the analysis was assessed by the strong metric distance $D_1$ [22] ($= 0.5R_{de}$ [20]) and the error bars were derived from the variance of $D_1$ [23]:

$$\text{Var}(D_1) = D_{1\text{min}} \times 0.76(4V_r/\Delta E)^{1/2} = 0.178 \times 0.073 = 0.013,$$

where $\Delta E$ is the cumulated energy range.

Error bars were determined by varying each parameter while keeping the others fixed. Although this does not take coupling between different parameters into account, the good agreement between the top-layer compositions derived by different methods indicates that such coupling [24] does not cause severe problems in our case. We also present results obtained by minimisation of Pendry’s $R$-factor, $R_P$ [25].

The analysis concerned a total of five layers including atomic positions (interlayer distances, buckling and lateral shifts consistent with the 2mm symmetry), plus the composition of eight different
sites (see Fig. 1). Including variations of the mean square displacements of atoms (isotropic vibrations) in the top two layers and the rigid shift of the energy-independent real part of the inner potential, this amounts to a total of 23 parameters.

In spite of the differences between the two independent analyses, the final results in Vienna and Grenoble show little dispersion (0.01–0.02 Å generally) for the vertical distances (Table 1). The differences are a little larger for in-plane displacements—pairing, to which LEED is less sensitive.

The atomic fractions are quite similar for the rows forming the (111) facets while we note some difference on the concentrations (generally less than 20%) of the buried rows: in one case only, for the deeper sites to which LEED is much less sensitive, we note a large difference. However this is quite acceptable considering that concentrations

<table>
<thead>
<tr>
<th>$R$-factor Method</th>
<th>LEED</th>
<th>GIXRD, $\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1g$</td>
<td>1.23 ± 0.03</td>
<td>1.24 ± 0.04</td>
</tr>
<tr>
<td>$R_{fg}$</td>
<td>1.36 ± 0.04</td>
<td>1.33 ± 0.04</td>
</tr>
<tr>
<td>$D_{1w}$</td>
<td>1.40 ± 0.04</td>
<td>1.39 ± 0.04</td>
</tr>
<tr>
<td>$R_{pw}$</td>
<td>1.23 ± 0.03</td>
<td>1.37 ± 0.03</td>
</tr>
<tr>
<td>$d_b$</td>
<td>1.365</td>
<td>0.04 ± 0.06</td>
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<tr>
<td>$\Delta Y_1$</td>
<td>0.04 ± 0.06</td>
<td>0.04 ± 0.04</td>
</tr>
<tr>
<td>$\Delta Y_2$</td>
<td>0.02 ± 0.06</td>
<td>0.04 ± 0.00</td>
</tr>
<tr>
<td>$\Delta Y_3$</td>
<td>0.01 ± 0.06</td>
<td>0.02 ± 0.00</td>
</tr>
<tr>
<td>$\Delta Z_{11}$</td>
<td>0.15 ± 0.04</td>
<td>0.18 ± 0.04</td>
</tr>
<tr>
<td>$\Delta Z_{21}$</td>
<td>0.15 ± 0.04</td>
<td>0.12 ± 0.05</td>
</tr>
<tr>
<td>$\Delta Z_{31}$</td>
<td>0.03 ± 0.03/0.05</td>
<td>0.04 ± 0.04</td>
</tr>
<tr>
<td>[at.% Pt]</td>
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<td>$C_4$</td>
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<td>$C_{52}$</td>
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<td>30 ± 30</td>
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<td>$C_{55}$</td>
<td>24</td>
<td>30 ± 30</td>
</tr>
<tr>
<td>$R_{min}$</td>
<td>0.177</td>
<td>0.297 ± 0.178</td>
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<tr>
<td>$\text{Var.} (D_1)$</td>
<td>0.013</td>
<td>0.296 ± 0.296</td>
</tr>
</tbody>
</table>

"g" and "w" stand for data analysis performed in Grenoble and Vienna respectively. All interlayer spacings $d_j$ are given with reference to the geometrical centre of the plane. $C_j$ is the Pt concentration of atom $j$ (when more than 1) in layer $i$. $\langle C \rangle$ is the average Pt concentration of the five surface layers. $C_i$ is the concentration of layer $i$ of the {111} facets (see inset of Fig. 7). The bulk parameters, $d_b$ and $C_b$, were kept fixed for the whole analysis.
are second order parameters with respect to atomic spacings (see below). For many parameters, the differences are larger between both $R$-factors than between both independent analyses but in no case do they exceed the error bars. However, the trends are essentially the same, with movements in the same directions and enrichment of the same order of magnitude all over the refined region. The ultimate spectra are displayed in Fig. 4 which shows that almost all structures are quite well described with some discrepancies regarding the relative intensities, however.

As all types of domains contribute to the integer order beams and since the presence of $(1 \times 2)$ areas might modify the overall result a few runs were performed with fractional $(1 \times 3)$ beams only: the impact on the parameter optima is extremely weak showing that mainly the $(1 \times 3)$ reconstruction
(and a few small (1 × 2) areas only) contributes to the intensities.

5.2. X-ray diffraction

The RT database comprises a total of 206 non-equivalent reflections plus a limited number of equivalent reflections (67): indeed, due to the sample shape and mounting, a large part of the reciprocal space was hidden. Among these 206 reflections we kept for refinement only the 142 non-equivalent ones belonging to fractional rods. The model search was realised using the ROD code [26] and based on a $\chi^2$ minimisation in the framework of the missing-row model described above. The structure factors extracted from the experimental data and the simulated ones for the optimum model are plotted in Fig. 5, showing quite good agreement between measured and calculated spectra. The error bars of the experimental structure factors take into account both the statistical errors when integrating the measured intensities as well as the differences in the measurements of the equivalent reflections. These error bars (Fig. 5)
are relatively large and moreover, the data set is small compared to the number of variables in the model: this gives rise to several close minima in \( \chi^2 \) resulting in large error bars in the structural parameters (see Table 1).

Optimising the same set of parameters as in LEED, we obtain a best fit \( \chi^2 = 2.1 \), and \( R = 0.078 \). The best model is clearly quite similar to the LEED one, showing the same major trends. However, in the details, some differences, commented below, do exist between both techniques.

### 6. Structural arrangement and composition

#### 6.1. Geometry

Table 1 displays the results of the quantitative analysis by LEED and X-rays. In the manner of the noble metals and alloys cited previously, the Pt\textsubscript{50}Rh\textsubscript{50}(110) surface suffers significant distortions down to the fifth layer due to the reduced coordination resulting from the missing rows. The most remarkable change in the geometry is the strong contraction (\( \sim -10\% \)) of the interlayer spacing between the top row and layer 2. While the next two spacings are shorter than in the bulk, the distance from the 4th to 5th layer (the first one with no atoms in contact with vacuum) is increased by \( \sim 2.5\% \). We detect buckling of the three layers containing more than one atom per unit cell as well lateral displacements. The corrugation is \( \Delta Z_1 = 0.17 \, \text{Å} \) and \( \Delta Z_4 = 0.13 \, \text{Å} \) in layer 3 and layer 4 and is still detectable in layer 5 (\( \Delta Z_5 \sim 0.04 \, \text{Å} \)). The atoms on the facets and close to the bottom of the valley (\( C_{32}, C_{42} \) and \( C_{32} \)) move outwards and lie above those that are buried below the first layer atoms (\( C_{31}, C_{41} \) and \( C_{51} \)).

In layers 2 and 3, the atoms that are not in a symmetrical position move also laterally (\( \Delta Y \sim 0.02–0.05 \, \text{Å} \)), towards the centre of the valleys as they do for the other \((1 \times 3)\) missing-row structures. Conversely, the (weak) horizontal displacement is in the opposite direction for layer 4 as shown simultaneously by LEED and grazing incidence X-ray diffraction (GIXRD).

The 5th layer contributes much less than the others to the non-integer rods and its parameters are quite roughly determined. In particular, we checked the pairing \( \Delta Y_3 \), which happens to be the largest one in the surface diffraction analysis of the Pt(1 1 0)-(1 \times 3) structure [14]. In fact \( \Delta Y_3 \) is found to be much smaller than the pairing in the 4th layer and was then neglected in the rest of the analysis in LEED and GIXRD as well. We remark that the in-plane displacements obtained by the LEED analysis are comparable to the error bars (or smaller) while the corresponding error bars are much smaller for the GIXRD analysis. This is not surprising as it is known that, for the in plane parameters, this technique gives better results than LEED [27]. In summary, a significant lateral shift (0.05 \( \text{Å} \)) is detected by GIXRD in layers 2 and 3 only and, generally speaking, atoms remain close to their 2D bulk positions.

There is one remarkable fact with the geometry extracted from GIXRD compared to that derived from LEED calculations, especially concerning the interlayer distances. Indeed, while the vertical shifts agree rather well in both methods—same trends regarding directions and very close values—it is striking that those interlayer spacings which come out large (small) with X-rays are comparatively small (large) in LEED, with quite significant absolute differences (0.04–0.13 \( \text{Å} \)): for instance \( d_{12} = 1.32 \, \text{Å} \) (GIXRD) against \( d_{12} = 1.23 \, \text{Å} \) (LEED) and \( d_{34} = 1.46 \, \text{Å} \) against \( d_{34} = 1.33 \, \text{Å} \). Similar remarks were made in the X-ray analysis of the \((1 \times 3)\) MR reconstruction of Pt(1 1 0) (see Table 2) [14] and in the LEED study of a much more simple structure, Pt\textsubscript{25}Co\textsubscript{75}(1 1 1) [28]. In the latter case, LEED predicted Pt atoms being localized \( \sim 0.1 \, \text{Å} \) above the Co ones in total agreement with STM findings while GIXRD failed, predicting Co \( \sim 0.1 \, \text{Å} \) above Pt.

One clear difference is that, in LEED, all integer and fractional beams were included in the calculation while superstructure rods only were taken into account in the GIXRD analysis. This may explain part of the disagreement as defects in the periodicity \((1 \times 2), (1 \times 4), \ldots\)—which are quite common in MR reconstructions—are included in LEED via the integer beams while they are not in the X-ray analysis, neither for the PtRh sample nor the Pt(1 1 0) surface [14]. We may add, that integer rods—not considered for the final GIXRD
results presented herein—worsen quite markedly the agreement when they are included in the optimisation process.

In the LEED analysis we find that, firstly, the fractional order beams considered separately lead to R-factors with the same order of magnitude ($D_1 = 0.178$ and $R_p = 0.314$) as those for the overall data set; secondly, optimisation runs starting with the X-ray optimum parameters yield fractional beams R-factors as high as $D_1 = 0.400$ and $R_p = 0.500$.

In other words, this difference in the data basis (fractional versus fractional + integer order) retained for LEED and X-ray cannot be assigned any responsibility for the observed shifts/inversions in the distances.

If, to calculate the structure factors, we fix the parameters to those derived from LEED we get a significantly worse agreement $\chi^2 = 8.4$ ($R = 0.15$) than letting them free (see above). Similarly the X-ray model yields higher metric distance values in the LEED calculations. There is apparently neither an obvious way to reduce the gap between both techniques nor any satisfactory explanation so far. The unique point we could make here is that, owing to the presence of Ta wires to fix the

<table>
<thead>
<tr>
<th></th>
<th>Pt(110), (1 × 3)</th>
<th>Pt$<em>{50}$Co$</em>{10}$, (1 × 3),</th>
<th>Pt$<em>{50}$Fe$</em>{50}$, (1 × 3),</th>
<th>Pt$<em>{50}$Rh$</em>{50}$, (1 × 3),</th>
<th>Pt$<em>{25}$Rh$</em>{75}$, (1 × 2),</th>
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<tbody>
<tr>
<td></td>
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<td>XRD</td>
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<td>LEED</td>
<td>LEED</td>
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<td>$d_{12}$ [Å]</td>
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<td></td>
<td>16</td>
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<td>1.48</td>
<td>1.33</td>
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<td>0.17</td>
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<td>$\Delta Z_2$</td>
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<td>0.31</td>
<td>0.20</td>
<td>0.12</td>
<td>-</td>
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<tr>
<td>$\Delta Z_3$</td>
<td>0.04</td>
<td>0.09</td>
<td>0.01(6)</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>$\Delta Z_4$</td>
<td>0.04</td>
<td>0.014</td>
<td>&lt;0.02</td>
<td>0.03</td>
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<tr>
<td>$\Delta Z_5$</td>
<td>0.01</td>
<td>0.029</td>
<td>0.00</td>
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</tr>
<tr>
<td>$C_1$ [% Pt]</td>
<td>-</td>
<td>-</td>
<td>92</td>
<td>91</td>
<td>82</td>
</tr>
<tr>
<td>$C_2$</td>
<td>-</td>
<td>-</td>
<td>94</td>
<td>83</td>
<td>84</td>
</tr>
<tr>
<td>$C_{31}$</td>
<td>-</td>
<td>-</td>
<td>36</td>
<td>37</td>
<td>48</td>
</tr>
<tr>
<td>$C_{32}$</td>
<td>-</td>
<td>-</td>
<td>93</td>
<td>98</td>
<td>90a</td>
</tr>
<tr>
<td>$C_{41}$</td>
<td>-</td>
<td>-</td>
<td>85</td>
<td>67</td>
<td>81</td>
</tr>
<tr>
<td>$C_{42}$</td>
<td>-</td>
<td>-</td>
<td>100a</td>
<td>95a</td>
<td>-</td>
</tr>
<tr>
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<td>-</td>
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<td>61</td>
</tr>
<tr>
<td>$C_{52}$</td>
<td>-</td>
<td>-</td>
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<td>82</td>
<td>26</td>
</tr>
<tr>
<td>$\langle C \rangle$</td>
<td>86</td>
<td>80</td>
<td>70</td>
<td>58</td>
<td>54</td>
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<tr>
<td>$C_{y'}$</td>
<td>94</td>
<td>91</td>
<td>85</td>
<td>88</td>
<td>88</td>
</tr>
<tr>
<td>$C_{y''}$</td>
<td>78</td>
<td>69</td>
<td>59</td>
<td>31</td>
<td>26</td>
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<tr>
<td>$r_i$ [Å]</td>
<td>1.342</td>
<td>1.332</td>
<td>1.347</td>
<td>1.356</td>
<td>1.350</td>
</tr>
<tr>
<td>$\Delta r_i/r_b [%]$</td>
<td>-3.2</td>
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<td>-2.9</td>
<td>-1.7</td>
<td>-1.1</td>
</tr>
<tr>
<td>$\Delta r_{2}/r_b$</td>
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<td>-0.6</td>
<td>-0.2</td>
<td>-0.1</td>
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<tr>
<td>$\Delta r_{31}/r_b$</td>
<td>0.28</td>
<td>-0.4</td>
<td>&lt;0.1</td>
<td>0.35</td>
<td>&lt;0.1</td>
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<td>$\Delta r_{32}/r_b$</td>
<td>2.2</td>
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<td>~0</td>
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<tr>
<td>$\Delta r_{41}/r_b$</td>
<td>1.4</td>
<td>-2.0</td>
<td>0.25</td>
<td>&lt;0.1</td>
<td>-</td>
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</table>

Interlayer distances are related to the geometrical centre of the plane. $r_{ij}$ is the average nearest-neighbour distances of atom $j$ in layer $i$ and $\Delta r_{ij}/r_i$ its variation relative to the bulk value of the corresponding alloys.

$a$ Denotes the row at the bottom of the valley.
sample and due to the grazing incidence angle, we could collect only 1/3 of the equivalent X-ray reflections. This could affect a little the measurements but we are not really convinced this explains why the XRD results depart somewhat from the LEED ones. Indeed, it is worth to note here that: (i) the LEED data for pure Pt(110) [17], with low $d_{12}$ and high $d_{23}$, are much closer to the theoretical results for (1 x 2) MR reconstructions, including today’s ab-initio calculations [29,30], than to the GIXRD data; (ii) the GIXRD data of the (1 x 2) do not show such a big difference to LEED (see Table 1 in Ref. [29]) as for the (1 x 3); (iii) in the case of Pt$_{32}$Co$_{75}$(111) where comparison is possible, GIXRD failed completely predicting the correct atom shifted outwards while LEED and STM lead to consistent pictures; (iv) the present LEED results give a coherent description of all (1 x 2) and (1 x 3) missing-row reconstructed surfaces (see Table 2 and Ref. [29]), with similar and gradually changed interlayer spacings (while varying $C_b$ and the alloyed element) whereas GIXRD results for Pt(110)-(1 x 3) and Pt$_{50}$Rh$_{50}$(110)-(1 x 3) are at odds with such a picture. For these reasons, the following discussion about vertical relaxation will be preferentially based on LEED results.

6.2. Composition

All rows exposed to vacuum exhibit large Pt enrichment: three of them—those forming the (111) microfacets—contain less than 10% Rh (averaged LEED data). Only the row at the bottom of the valley shows a comparatively high Rh fraction (20–50% depending on the R-factor and method). Without any exception, all buried rows are Pt depleted which reminds of a trend already observed in many alloy equivalent surfaces (Fig. 6).

We may discuss the composition in terms of atomic (110) layers but probably more significant is a picture in terms of the {111} facets, which are the areas actually exposed to vacuum and adsorption [4,7]. This is all the more justified since, in non-reconstructed (110) surfaces, segregation reversal is the rule (pure or almost pure Co or Ni top layer for Pt$_{32}$Co$_{75}$ [8], Pt$_{50}$Ni$_{50}$ [11,31], Pt$_{10}$Ni$_{90}$(110) [10,12], Pt$_{25}$Ni$_{75}$(110) [13]) in contrast with the present situation where Pt covers most of the exposed surface. Considering these {111} surfaces (see Fig. 1a), the layer-averaged concentrations (see inset in Fig. 7) read $\langle C_y \rangle \approx \frac{89}{31}\%$ Pt from surface to bulk.

The surface is markedly enriched with Pt, the second layer shows a marked depletion with respect to the bulk and the third layer exhibits the same tendency although less significant owing to the reduced sensitivity for atoms in the fifth and sixth atomic layers (Fig. 7). The average concentration of the slab made of the five external layers amounts to $\langle C \rangle \sim 58\%$ Pt which represents a weak enrichment with respect to the equivmolar bulk layers, most of the extra Pt segregating to the valley slopes. As we already considered for Pt$_{90}$Co$_{10}$(110) and Pt$_{25}$Rh$_{75}$(110) [3,7], it seems that this surface Pt enrichment is crucial for the missing-row reconstruction and vice versa: this is consistent with the above remark that those (110) surfaces which do not reconstruct are instead enriched in the light (and small-size) element, Ni or Co.
For the special case of the outermost row concentration, within reach of all methods, we find that they agree quite reasonably ($C_1 = 92, 88, 86, 94$ for LEED, GIXRD, STM and LEIS respectively). We may also point out that the LEIS result for the facet-averaged concentration ($C_V = 87\%$) ends within 1\% of the LEED and GIXRD results ($C_V = 88\%$), which is a nice confirmation of the result. With regard to the other individual rows, LEED and GIXRD agree fairly well, the largest difference, 17\% Pt, occurring for the buried atoms; they are even closer if we consider the (1 1 1) like surface for which the discrepancy in the layers concentrations is 5\% at most (see Table 1).

In spite of some quantitative differences, LEIS, GIXRD and LEED result in the same picture as to chemical parameters of the exposed rows.

6.3. Quality of the agreement and error bars

Fig. 6 and Table 1 show that in spite of minor differences in the individual rows, both LEED analyses and both $R$-factors yield quite close pictures regarding the concentrations and the geometry. At their minimum, the LEED $R$-factors in Vienna and Grenoble have values ($D_1 = 0.177, R_p = 0.296$) quite satisfactory for this type of surface reconstruction as compared for instance to pure Pt(1 1 0) [17] ($R_p = 0.35$), Pt$_{80}$Fe$_{20}$ [5] ($D_1 = 0.18, R_p = 0.34$) or Pt$_{90}$Co$_{10}$(1 1 0) [7] ($R_p = 0.28$) which all three display similar (1 x 3) missing-row arrangements. In comparison, the agreement is better ($R_p = 0.24$) for the (1 x 2) missing-row structure of the closely related Pt$_{33}$Rh$_{67}$(1 1 0) surface where, however, the variations with respect to bulk values concern three layers only instead of five in the present instance [3].

Table 1 also displays the error bars derived from the variance of $D_1$. They happen to be quite reasonable for the geometrical parameters although they are large if compared to non-reconstructed surfaces. They are however similar to those obtained for the equivalent (1 x 3) missing-row reconstruction of Pt$_{90}$Co$_{10}$(1 1 0) [7]. Regarding the concentrations, the present analysis leads to larger errors. These large values are due to the reduced atomic density (33\% and 66\% respectively in layers 1 and 2) with respect to complete layers and, above all, to the fact that Pt and Rh have rather similar scattering factors as compared to alloys of Pt with 3d metals (PtFe, PtCo, PtNi).

We wish to take this opportunity to point out that $R_p$ behaves somewhat in a strange fashion for the low sensitivity parameters such as concentrations: while $D_1$, for instance, has a nice and regular parabolic shape around the minimum, $R_p$ exhibits spurious fluctuations which result in less well defined minima in the present instance and in larger dispersion of the optima among beams and subsets [32]. This may explain, at least partially, some of the differences observed in the optima from $R_p$ and $D_1$ and why $R_p$ is given mainly for comparison to others works.

More generally, the error bars are larger for the atoms which are buried such as $C_{31}$ and $C_{32}$ (±50 and 68 respectively) while those exposed to vacuum ($C_1, C_2, C_3$) have much smaller ones: this is fully consistent, in a {111}-layers picture, with error bars increasing with depth.

Clearly, the limited agreement also originates from the imperfections of the surface (domain size, step density, presence of small (1 x 2) and (1 x 4)
areas) as exposed above, but not only. In previous analyses of missing-row reconstructions [4, 7] we have proposed, following others [17], that the remaining discrepancies are partially due to the anisotropic character of the reconstruction with dense protruding rows at the top of the valleys. This makes the isotropic thermal vibrations—considered in most LEED codes—a crude model. This also applies here also and may be, at least to some degree, the origin of the moderate agreement.

Nevertheless, the coherence of the responses of two—if not four—different techniques is a token of the validity of the conclusions.

7. Discussion and conclusions

From the similarities in the LEED patterns, \( I(V) \) spectra, bulk phases and STM images, it was not difficult to predict that, beyond the common missing-row picture, the atomic arrangement would have strong analogies with \( \text{Pt}(110) \) and Pt based alloy \( (110) \) surface structures with fcc like bulk phases.

The present results together with those obtained on \( \text{Pt}–\text{Co} \) and \( \text{Pt}–\text{Fe} \) alloys allow to draw some general rules regarding the missing-row reconstruction (see Table 2) irrespective of the periodicity, \( (1 \times 2) \) or \( (1 \times 3) \). In particular all equivalent sites behave in the same manner with respect to segregation, be it enrichment or depletion, which leads to the following:

- General Pt enrichment of the \{111\} facets. Indeed, without any exception, all sites exposed to vacuum have larger Pt concentration than the bulk. We also note that the larger the bulk concentration the larger the concentration of the atoms down the valley, a remark which also applies to the average composition of the facets, \( C_i \) (Table 2 and Fig. 7).

- Pt enrichment of the top row. \( C_1 \) is larger than 80% in all cases, with about the same amount (or a little less) than the other exposed rows of the \{111\} facets.

- Another common point to these MR structures is that the largest Pt depletion occurs on the buried row of layer 3 and 4 \( (C_{31}, C_{34}) \), immediately below the protruding row of layer 1 or in contact with the facet rows where large Pt segregation is observed \( (C_2, C_{32}) \). This illustrates nicely the usual trend of Fe, Co and Ni and, to a lesser extent, of Rh (see Table 2 of Ref. [28]) to be surrounded by the other species. Placing small atoms directly beneath the first-layer atoms is also favourable because it allows easier inwards relaxation of the first-layer Pt atoms.

- Considering the \{111\} layers, these surfaces reproduce quite nicely the well know trend of the same Pt–Me(111) surfaces; a surface layer enriched with Pt followed by a depleted layer and a gradual approach towards the bulk value (Fig. 8).

- For both \( \text{Pt}_{25}\text{Rh}_{75}(110)-(1\times2) \) and \( \text{Pt}_{50}\text{Rh}_{50}-(110)-(1\times3) \), the room temperature reconstruction is accompanied by a general Pt enrichment of the selvedge (five outermost layers for the \( (1 \times 3) \)) as the result of a gradual increase of the averaged Pt concentration \( (C_i) \) of each \{111\}-like layer. We wish to point out here that this overall enrichment is proportionally larger for the short period \( (1 \times 2) \) reconstruction \( (C_i/C_{\text{bulk}} = 19\% \text{ Pt}) \), than for the \( (1 \times 3) \) \( (C_i/C_{\text{bulk}} = 8\%) \). Table 2 reveals that this

![Fig. 8. Oscillating concentration profiles (average concentrations, \( C_i \), of the \{111\} facets) for \( \text{Pt}_{90}\text{Co}_{10}(110) \) [7], \( \text{Pt}_{90}\text{Fe}_{20}(110) \) [6] and \( \text{Pt}_{50}\text{Rh}_{50}(110)-(1 \times 3) \).](image)
trend is more general and applies also to the other MR reconstructions. In fact, $\langle C \rangle - C_{\text{bulk}}$ decreases regularly with $C_{\text{bulk}}$ so that the marked enrichment of the top layer facets at 25% turns into equilibrium around 80%.

In spite of quantitative differences naturally expected due to the differences in the element mixed with Pt (Rh is only 3% smaller than Pt while the difference is 10% for Co and Fe) and bulk composition, the analogy is also striking on the structural point of view since one notes:

- A strong contraction of the first interlayer distance. This contraction with respect to the bulk distance (LEED results) increases quite regularly with the bulk concentration to end up around 20% for pure Pt(110): the lower the Pt bulk content and the top layer concentration, the larger the distance.
- Buckling in all layers where symmetry allows. The corrugation decreases with distance from the surface, and the atoms closest to the valley are higher than the others.
- Pairing (0.02–0.05 Å in layer 2, 0.01–0.05 Å in layer 3) is the rule, the atoms moving systematically towards the valley. The trend is less clear in deeper layers where PtRh surfaces ((1 × 2) and (1 × 3)) give rise to very weak lateral shift in the opposite direction as the others but owing to the low sensitivity it may well be just noise.

The case of (110) alloy surfaces is intriguing: indeed they behave quite differently depending on the composition: at low Pt concentrations they keep the usual unreconstructed termination of bulk fcc, while in contrast they yield the distorted surfaces with MR reconstruction at high Pt concentration. The limit between both atomic arrangements varies with the chemical element alloyed with Pt and is directly related to the Pt enrichment in the surface layer and to the atomic radius of the second metal. For instance Pt$_{50}$Ni$_{50}$(110), with a similar bulk structure and the same Pt bulk concentration as Pt$_{50}$Rh$_{50}$ does not reconstruct and yields segregation inversion with a pure Ni layer on top instead of Pt rich {111} facets.

In fact, the MR reconstruction is linked to the well-known trend of noble metals, Pt, Au, to increase the atomic density via formation of {111} facets with (1 × 2) or (1 × 3) periodicity. As to which is most stable, the former or the latter, the question has not been really solved yet.

The contraction (expansion) of metal atoms in the top two layers (deeper layers) which accompanies the MR reconstruction is qualitatively understood in relation to the coordination number: while bulk atoms have full coordination (12 neighbours) the atoms in the ridges and on the facets have 7 and 9 neighbours, respectively [14]. Coupled with the pairing of the even layers and buckling of the odd ones, the first interlayer distance contraction yields strongly modified nearest-neighbour (nn) distances for the outer atoms. This is particularly true for the atoms on the ridges as already shown for pure Pt(110)-(1 × 2) and (1 × 3) (see Tables 2 and 4 of Ref. [17]). For the latter, the average contraction (LEED) of the low coordinated atoms is $\Delta r_1/r_b = 3.2\%$ while it is 0.1% for atoms in the centre of the facet (see Table 2).

For the alloys, we observe that the average nn distance $r_1$ is always significantly smaller than the bulk alloy distance $d_b$ (Table 2). Ligand effects, which apply here too, are an important parameter for chemical or catalytic properties of alloys. We have shown that Pt sites play a crucial role for adsorption in the case of PtCo(111) [33]. In the case of the (110) orientation, the contraction of the Pt sites may also modulate drastically these properties: in this respect, we note that, within 1%, $r_1$ is the same for all the alloys considered, irrespective of the periodicity. This is not surprising, remembering that the Pt concentration in the first two layers is essentially the same for all the alloys (except for Pt$_{25}$Rh$_{75}$). This almost constant value derives from the balance between two competing effects: the larger the lattice parameter, the lower the interlayer spacing $d_{12}$, at least for this type of alloys. This might be a fundamental factor in the reconstruction mechanism.

Simultaneously to this the overall trend towards increased contraction with increased Pt concentration, the relative Pt enrichment of the surface region, $\langle C \rangle - C_b$, shifts smoothly from large en-
richment for Pt_{25}Rh_{75} (19%) to weak depletion (−4%) in the case of Pt_{90}Co_{10}.

Although the details of the structure and concentrations may be questionable in particular for deep layers, the overall picture of this missing-row reconstruction is well established with consistent conclusions from four different techniques.

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References