Pt_xGd alloy formation on Pt(111): Preparation and structural characterization

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Abstract

Pt_xGd single crystals have been prepared in ultra high vacuum (UHV). This alloy shows promising catalytic properties for the oxygen reduction reaction. The samples were prepared by using vacuum deposition of a thick layer of Gd on a sputter cleaned Pt(111) single crystal, resulting in a ~63 nm thick alloy layer. Subsequently the surfaces were characterized using X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), ion scattering spectroscopy (ISS) and temperature programmed desorption (TPD) of CO. A Pt terminated alloy was observed upon annealing the sample to 600 °C. The LEED and synchrotron XRD experiments have shown that a slightly compressed (2×2) alloy appear. The alloy film followed the orientation of the Pt(111) substrate half the time, otherwise it was rotated by 30°. The TPD spectra show a well-defined peak shifted down 200 °C in temperature. The crystal structure of the alloy was investigated using ex-situ X-ray diffraction experiments, which revealed an in-plane compression and a complicated stacking sequence. The crystallites in the crystal are very small, and a high degree of twinning by merohedry was observed.

Keywords: Platinum alloys, Single crystals, X-ray diffraction, Alloy formation

1. Introduction

One of the most promising technologies for utilizing the energy stored in hydrogen is the low temperature polymer electrolyte membrane fuel cell (PEMFC). However, as a consequence of a large potential loss on the cathode these devices require a large amount of Pt to catalyze the Oxygen Reduction Reaction (ORR). To lower the Pt loading and improve the activity, Pt based alloys can be used instead of pure Pt [1–6]. However, bimetallic alloys tend to dealloy in the acidic environment in a fuel cell, causing the catalyst to degrade [7–9]. More recently we have investigated platinum and rare earth element bimetallic alloys because of their large negative heat of formation, which may provide a catalyst that is less prone to electrochemical dealloying

[10–12]. These alloys show a high activity for the ORR, and Pt_xGd in particular exhibit an exceptionally high activity for oxygen reduction, both in the polycrystalline form and the nanoparticulate form [12–14].

Gd modified Pt(111) single crystals have been investigated in order to understand the origin of the enhanced activity of this alloy. This article contains a thorough description of the alloy prepared in UHV combined with investigations of the crystal structure. Characterizing the alloy and its structural motifs is imperative for understanding the highly active Pt overlayer surface that forms during ORR [10, 12, 14–16].

The ideal catalyst for ORR will have a slightly weaker reactivity than Pt(111), and bind oxygen 0.2 eV weaker [17, 18]. To probe the reactivity of the surface, CO temperature programmed desorption experiments have been performed. Yates was amongst the pioneers of this techniques, which his group used on single crystals to study the dynamics of molecules, the effect of steps on the reactivity of Pt(112) [19], and reaction

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pathways on Ni(111) [20].

X-ray diffraction experiments made on polycrystalline Pt₅Gd have shown that this alloy has a large unit cell with a complicated stacking [21, 22]. Furthermore, these studies never found the crystal structure for Pt₅Gd using powder samples. In this article, we demonstrate how we can determine the space group, unit cell, and structural motifs behind a Pt-Pt compression using a 3-dimensional diffraction pattern. Due to the complicated stacking expected for this alloy, single crystal diffraction is essential, since it provides much more structural information than powder diffraction.

We publish this work in memory of John T. Yates and his great contribution to the field of surface science.

2. Experimental setup

The sample preparation and the UHV characterization were performed in a vacuum chamber with a base pressure of $1.0 \cdot 10^{-10}$ Torr. The chamber is equipped with standard UHV surface science techniques; X-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), low energy electron diffraction (LEED), and a quadrupole mass spectrometer for temperature programmed desorption (TPD). ISS is performed using He⁺ ions accelerated over a voltage of 1.25 kV. The XPS experiments were performed using K_α radiation from a Mg anode (1253.4 eV).

The sample, a Pt(111) single crystal, 5 mm in diameter and 3 mm thick, was supplied by MaTecK, GmbH, Germany. The sample was mounted in a hairpin shaped tungsten wire which was then mounted onto the feed-through on the manipulator end [23]. The temperature is measured using a type K thermocouple. The sample can be resistively heated at a linear ramp regulated by a PID controller, and cooled to $T = -190^\circ\text{C}$ using liquid nitrogen. The main chamber is equipped with a water cooled metal Gd evaporator and a quartz crystal microbalance (QCM), which makes it possible to evaporate Gd on the surface of the sample at a well known evaporation rate. The evaporator was made by cutting flakes of a Gd foil and attaching them to a coil shaped 0.25 mm 99.95 % tungsten wire. The Gd flakes were cut from a 0.127 mm 99.9 % Gd foil supplied by Alfa Aesar.

After the Gd/Pt(111) single crystal was made with a thick alloy in the UHV chamber at DTU, it was transported to the Stanford Synchrotron Radiation Light-source (SSRL). The sample was transported and measured in air, and no surface cleaning was necessary since the alloy phase was quite thick (estimated to be ~ 63 nm) and protected from oxidation by the Pt overlayer. The

diffraction experiments were carried out at beam line 7-2, which was equipped with a Huber six-circle (4+2) diffractometer and a Dectris Pilatus 300K imaging detector. The diffractometer stage was equipped with a goniometer head that allowed the crystal surface normal to be aligned to the phi rotation axis using a laser. All the data was acquired at a fixed incidence angle of 0.2° to maximize surface sensitivity, and the photon energy was set to 11.0 keV to avoid fluorescence background from the Pt. A sketch of the setup is seen in Figure 1 [24]. At each detector position a circular diffraction pattern from a polycrystalline LaB₆ sample was recorded, so that the position of the detector could be calculated. Data was acquired by rotating the crystal in steps of 0.2° , and a rocking scan was performed in each spot. This was repeated using 6 different positions of the detector. The acquired diffraction data was stitched together to form a 3-dimensional image of parts of the Q -space, and the intensity has been corrected for the Lorentz factor, polarization, and geometrical effects using MatLab scripts developed by the authors.

Figure 1: A sketch of the experimental setup used for the X-ray diffraction measurements. The incidence angle was fixed at $\alpha = 0.2^\circ$ for all measurements. The whole reciprocal space is reconstructed by rotating the sample around its surface normal and stitching each slice of data. The image is from [24].

3. Results

3.1. Alloy formation

Earlier experiments have shown that it is possible to prepare a well-organized crystalline structure by vacuum deposition of monolayers of lanthanide metals on a sputter cleaned Pt single crystal [25–28]. Our experiments with deposition of thick layers of Y on Pt(111) have shown that it is possible to simulate a crystal that behaves like a single crystal [15]. On the basis of these promising results, we initiated experiments on Gd modified Pt(111) single crystals.

3.1.1. Creating a near surface alloy

To probe whether Gd and Pt would form an alloy, a thin layer of 2 nm Gd was deposited on a sputter cleaned, annealed Pt(111) surface. XPS measurements performed after the deposition showed that the Gd was partially oxidized, see S.I. Section 1. During the evaporation an increase in the pressure to approximately $1.0 \cdot 10^{-9}$ mbar due to degasing of the evaporator could not be avoided. Gadolinium has a high affinity to oxygen ($\Delta H = 1819.6$ kJ/mol, corresponding to an energy gain of 9.4 eV per Gd atom for $2\text{Gd} + 1.5\text{O}_2 \rightarrow \text{Gd}_2\text{O}_3$), and can oxidize even under UHV conditions [29]. To remove the traces of gadolinium oxide, the sample was gently sputtered using Ar ions for 10 min. The composition of the atoms in the surface of the sample was probed using ISS immediately after. The sample was then heated in steps of 25 °C and the composition of the surface was evaluated after each heating step. ISS spectra for representative temperatures can be seen in Figure 2. At $T = 200$ °C the spectrum is dominated by Gd, at $T = 500$ °C the Pt signal becomes visible, and at $T = 800$ °C the surface is completely dominated by Pt, indicating a formation of a Pt_xGd alloy terminated by a Pt overlayer.

Figure 2: ISS spectra measured at different temperatures. At $T = 200$ °C the sample is dominated by Gd and only a small amount of Pt can be seen, at $T = 500$ °C the platinum signal becomes more pronounced, and at $T = 800$ °C the Pt signal becomes dominant indicating the formation of a Pt overlayer.

In Figure 3 the relative intensity of the Gd signal can be seen as a function of temperature. It can be seen that the amount of Gd in the surface drops rapidly at $T = 450$ °C, and at temperatures above $T = 500$ °C, the spectra are dominated by Pt, indicating inter-diffusion of Gd and the formation of a Pt overlayer. The alloying process is sketched in Figure 4.

Figure 3: The 'Gd' to the 'Gd+Pt' ratio probed with ISS as a function of temperature. The intensities have been found by comparing the peak intensities. No sensitivity factors have been used and hence the ratio can only be considered qualitatively. At $T = 450$ °C the amount of Gd decreases significantly indicating alloy formation terminated by a Pt overlayer.

XPS was performed to verify that the Gd has merged to the subsurface layer, and that the decrease in the Gd intensity is not a consequence of He^+ sputtering of the gadolinium atoms in the surface during the ISS experiment, see Figure 5. Furthermore, an overview spectrum can be seen in S.I. Section 1. From the XPS measurement, it can be seen that the gadolinium is still present, indicating that it has merged to the subsurface region and has created a near surface alloy (NSA). It is possible to calculate the stoichiometry of the alloy under the assumption that the surface is terminated by a single layer of platinum [30]. The quantification of the XPS spectrum can be seen in Table 1

Pt [%]	Gd [%]	x for $\text{Pt}/\text{Pt}_x\text{Gd}$
89.7	10.3	6.9

Table 1: Concentrations of the different elements in the Gd/Pt(111) quantified with XPS after the gadolinium deposition and annealing to 800 °C.

To probe the reactivity of the thin Pt_xGd alloy terminated by Pt, CO TPD was performed on a CO saturated surface. $2.0 \cdot 10^{-7}$ torr CO was dosed for 30 minutes while the sample was cooled from 400 °C to -190 °C, corresponding to a dosage of 360 L. The sample was heated at a constant rate of 2 °C/s during the TPD ex-

Figure 4: The deposition process. Gd is deposited on the surface of Pt(111) at room temperature. At this temperature the Gd is not mobile. After heating up the crystal Gd becomes mobile and migrate to the subsurface region and a Pt surface monolayer is formed.

Figure 5: XPS performed after Gd deposition and annealing to 800 °C.

Figure 6: TPDs on CO saturated surfaces. Blue curve: TPD made on the thin, near surface alloy of Gd/Pt(111), red curve TPD made on the bulk alloy, black curve TPD made on a sputter cleaned, annealed Pt(111) surface. The TPDs are made at a constant heating rate of 2 °C/s.

periments. The CO TPD can be seen in Figure 6 where it is compared to a CO TPD made on a CO saturated Pt(111) surface. The experiment was performed several times, and has shown a high degree of reproducibility. This indicates that there were no dissociation of CO. In the CO TPD made on the Gd/Pt(111) sample a sharp peak appears at $T = -10$ °C. This peak has a shoulder to higher temperatures at $T = 0$ °C, and a less pronounced shoulder to lower temperatures at $T = -60$ °C. The integrated intensity of the desorption peaks were calculated to evaluate the amount of CO molecules adsorbed on the surface during the TPD experiments. The coverage of the sample can be evaluated by comparing this value to the integrated intensity of the desorption peak from the Pt(111) sample, since the behavior of CO on clean Pt(111) surfaces has been studied extensively over the last decades [31–36]. For a perfect Pt(111) single crystal the CO saturation coverage is $\theta = 0.68$ [32].

By comparing the integrated desorption peaks we determine a CO saturation coverage of $\theta = 0.54 \pm 0.03$ on Gd/Pt(111). We anticipate that the variations in the measured coverage is mainly a consequence of small variations in the sample position relative to the mass spectrometer.

3.1.2. Simulating a bulk alloy

To simulate the behavior of a bulk alloy, a thick layer of Gd was deposited on a sputter cleaned, annealed Pt(111) surface. A thick layer of (200 ± 50) Gd was deposited on a sample heated to a temperature of 800 °C in UHV. This temperature is well above the mobility temperature and hence we anticipate that a platinum overlayer will form instantaneously which will protect the Gd from oxidation. The stoichiometry of the alloy

was evaluated using XPS, see Table 2. Traces of oxygen were seen in the XPS spectra, see Figure 7, indicating the formation of gadolinium oxide. To remove this, the sample was sputtered gently using Ar-ions while the sample was kept at 800 °C. The amounts of oxygen and

Figure 7: Blue: XPS overview spectrum made after the deposition of gadolinium at 800 °C. Oxygen can be seen in this spectrum indicating the formation of gadolinium oxide. Red: XPS spectrum made on the sample after a light sputtering at 800 °C. After the sputtering, the oxygen signal is close to the detection limit.

gadolinium have decreased significantly after the sputtering, which implies that a layer of gadolinium oxide has been formed on the surface during the evaporation, and that the sputtering procedure has removed this. The stoichiometry of the alloy has been evaluated assuming that the platinum skin consists of a single layer of atomic platinum of thickness $d = 2.28$ [30], see Table 2.

	Pt [%]	Gd [%]	O [%]	x for $\text{Pt}_x\text{Pt}_y\text{Gd}$
Before	74.0	17.4	8.5	3.2
After	87.4	12.5	0.1	5.5

Table 2: Concentrations of the different elements in the Gd/Pt(111) quantified with XPS after the gadolinium deposition. The measurements were made before and after Ar sputtering at 800 °C.

From the calculated Gd concentration, it is most likely that the crystal has formed Pt_5Gd , which is the most platinum rich, stable Pt_xGd alloy [37]. The composition of the surface layer was measured using ISS, see Figure 8. Gd was not seen in the ISS spectrum after the deposition, indicating the formation of a Pt overlayer.

The reactivity of this surface was probed using CO TPD experiments using the same experimental conditions as for the thin alloy. The sample was saturated with CO, cooled using liquid nitrogen, and heated using

Figure 8: ISS before and after the deposition. Gd was not seen in the spectrum measured after the deposition, indicating the existence of a Pt overlayer.

a constant heating rate of 2 °C/s, see Figure 6. The TPD experiments were repeated several times showing a high degree of reproducibility. From the integrated intensity of the desorption peak the CO saturation coverage of this surface is $\theta = 0.58 \pm 0.02$.

LEED was performed to evaluate the crystal structure of the Gd/Pt(111) sample. This was made on the clean Pt(111) surface before the Gd deposition, and after the deposition and annealing, see Figure 9. A well-defined diffraction pattern appears after the deposition of Gd, indicating that a well-defined, crystalline surface has been formed. The structure of the Gd/Pt(111) surface is hexagonal and show a (1.90×1.90) structure, not rotated with respect to the platinum substrate. The position of the diffraction peak can be estimated within a resolution of 2 %. Gd/Pt(111) samples have been prepared using this procedure 5 times. The lattice constant of the observed structures is always the same, but the rotation could vary; the alloy film followed the orientation of the Pt(111) substrate half the time, otherwise it was rotated by 30°, see S.I. Section 4. This indicates that these two configurations are equivalent or extremely close in energy. We will consider this further in the discussion section.

3.2. X-ray diffraction experiments

The 3-dimensional Q -space was investigated, and it was immediately seen that the alloy has a hexagonal symmetry in the plane of the crystal surface. Figure 10 shows the diffraction pattern integrated along the L-direction, the surface normal. The arrows show the in-plane H and K crystal lattice vectors, and the L lattice vector is perpendicular to the figure plane. The red

Figure 9: *Top: A LEED pattern made on a sputter cleaned, annealed Pt(111) surface. Bottom: LEED pattern made on the prepared Gd/Pt(111) sample. The colors have been inverted for clarity. The surface structure forms a (1.90×1.90) structure not rotated with respect to the Pt substrate.*

circles show the diffraction peaks from the Pt_xGd alloy, whereas the black circles show the diffraction peaks from the Pt(111) substrate. The Pt surface monolayer may have a different crystal structure than the rest of the alloy, but the sensitivity of this XRD experiment is not high enough to detect a single monolayer. A large number of super-spots are seen, indicating a high degree of twinning. Besides twinning by merohedry (overlapping diffraction spots) indicated by the super-spots some non-merohedral twins are present, since many of the diffraction spots are split into 3 spots. This peak splitting indicating domains in the alloy is more clearly seen in Figure 11, showing a zoom of the white square in Figure 10. This non-merohedral twinning shows a small rotation around the surface normal, and is caused by separate domains in the alloy only, since the Pt(111) substrate does not show any splitting. Unfortunately these

non-merohedral twinned peaks are too close to rigorously separate, and in the further data processing they have all been included in a single integrated intensity.

(a) *Logarithmic scale.*

(b) *Linear scale.*

Figure 10: *The XRD intensity integrated along the surface normal, along the L lattice vector. The arrows show the in-plane crystal lattice vectors H and K, the red circles show the diffraction peaks from the Pt_xGd alloy, and the black circles show the diffraction peaks from the Pt(111) substrate. Many super-spots are seen, indicating a high degree of twinning. Furthermore non-merohedral twinning is seen as the spots are split in 3, and this is shown by a zoom of the white square in Figure 11. In (a) the color scale is logarithmic to show more features, and the intensity ranges 4 orders of magnitude. In (b) the color scale is linear and the maximum is set to 1/4 of the maximum intensity of the peaks.*

Figure 11: The alloy splitting in 3 domains is clearly seen in this surface plot, showing a zoom in of the white square in Figure 10. The 3 large peaks are from the alloy and the weak peak closest is the Pt(111) substrate. The substrate peak does show some broadening in the left-right direction, but there is no splitting as seen in the alloy.

The hexagonal unit cell dimensions were found by fitting a pseudo-Voigt peak shape to the positions of the brightest alloy peaks. These positions in Q -space were then calibrated using the Pt(111) substrate diffraction peaks, and small corrections on the order of 1% were made, since the detector positioning method using the LaB₆ sample is not perfect. In the hexagonal unit cell the parameters are $a = 5.3309 \pm 0.0008 \text{ \AA}$ and $c = 40.358 \pm 0.012 \text{ \AA}$. Furthermore from the width (full width at half max, FWHM) of the peaks the crystallite sizes are estimated using Scherrer's formula [38], and using a shape factor of 1 the in-plane size is estimated to be 22 nm and out-of-plane size 12 nm. This small crystallite size is consistent with the high number of super-spots seen, since a typical beam coherence length on the order of a μm will illuminate a large number of domains coherently. The broadening of the peaks from the beam coherence has not been taken into account, since the crystal broadening is much larger.

The main alloy diffraction peaks were indexed, and the intensity was integrated by summing the voxels around each diffraction peak. The noise was assumed to be 10 counts (out of a maximum count of 1,000,000) per voxel. Integrated intensity of the peaks was calculated by summing the intensities in the voxels around the area covering the brightest peak and a depth large enough to cover all 3 domains. Uncertainty on the intensity measurement were estimated as the square root of 10 times

the number of voxels contributing to the integrated peak. The range of diffraction peaks in-plane was from $(H,K) = (1,0)$ to $(2,1)$, and the out-of-plane range was $L = 1$ to 24. Due to the low incidence angle the specular diffraction spots are unavailable, and for the $\langle 10L \rangle$ peaks the maximum L was 21 or 22. This leads to a total of 705 diffraction peaks indexed. The measured intensities and the estimated uncertainties from noise are found in S.I. Tables 1, 2, 3, 4, and 5, where H and K are multiples of the two reciprocal lattice vectors shown in Figure 10 and L is multiple of the reciprocal lattice vector pointing out of the plane in the same figure.

Space group determination was done using the program SHELXT, part of the SHELX crystal structure determination and refinement package [39]. The best fit to the presented data is R3m, spacegroup 160, which has a rhombohedral symmetry. In here, we use the hexagonal axes to represent the rhombohedral lattice to make comparison to the Pt(111) substrate more intuitive. With inspiration from the high temperature Pd₅Ce [40] and Cu₅Ca [22] structures, an initial guess was made. The height of the unit cell (c axis) is consistent with 18 Pt(111) like atomic layers. The rhombohedral symmetry reduces the asymmetric cell to $1/3$ c axis height, i.e., 6 Pt(111) like layers. The initial guess for the asymmetric cell is shown in Figure 12. The lines show the unit cell in-plane, and the z -value indicates the relative z -coordinate of the given layer. In this structure three different types of layers are seen. Gd atoms are only located in the 2nd and the 6th layers (H_1 and H_3) and they are ordered with Pt in 2:1 (Pt₂Gd), and 1:2 (PtGd₂) ratios. The layers above or below the Gd containing layers, i.e., 1st, 3rd, and the 5th layers, have vacancies in the hexagonal net just above or below the Gd atoms, forming a "kagome" like net (K_1 , K_2 , and K_3). The 4th layer in the asymmetric cell (H_2) is a Pt only hexagonal net with no vacancies. The atoms in the kagome layers are on a 9b Wyckoff site; whereas the atoms of both types of the hexagonal layers are on a 3a Wyckoff site. There are 12 unique atoms in the asymmetric unit cell with 15 refinable position parameters, and the full unit cell has 54 atoms. Ordering of the Gd atoms and the corresponding vacancies in the adjacent kagome layers presumably helps to accommodate the larger Gd ion.

To optimize the guessed structure the program SHELXL was used, which was used with a least-squared fitting routine. As an input it takes the unique atomic positions and optimizes them against the measured peaks. Out of the 705 measured peaks, 55 unique peaks were found for this space group. The program has an option for handling simple twinning, but it was not possible to get any stable fits considering different kind

Figure 12: The first 9 layers out of 18 of the initial structure guess, the grey spheres are Pt and green spheres are Gd. Due to the rhombohedral symmetry the 6 first layers repeat above, but are shifted by one atom, as shown here. The lines show the unit cell in-plane, and the z -coordinate gives the relative z -position of the given layer. Three types of layers are seen, the first layer is a kagome type layer consisting only of Pt, and it has a void that can accommodate the larger Gd in layer above or below. The other layers are hexagonal and are either pure Pt (H_2) or have a varying Pt-Gd stoichiometry. To distinguish the layers the kagome layers are labeled by K and the hexagonal layers are labeled H, and the * denotes symmetrically equivalent planes. The unique atoms in the asymmetrical unit cell have been labeled as well.

of twins, both 60° rotated twins and obverse/reverse rhombohedral twinning was attempted. Assuming the trial structure described above, the structure factors for a 60° rotated twin was calculated and all peaks that contribute to this twin were removed from the raw data. A total of 235 diffraction peaks were removed, leaving 470 peaks of which 47 are unique. Because of the complexity of structure and relatively few unique reflections, first set of refinements were performed by fixing the Debye-Waller factors to being isotropic at a value of $0.02 \text{ \AA}^2$, and constraining Pt-Pt distances to be approximately equal. In the subsequent refinements, Pt-Pt distance constraints were removed, to achieve a stable refinement with R1 of 0.57 (0 being a perfect fit). To understand the reason for the relatively large R-factor, the calculated and measured structure factors were plotted against the scattering vector Q , see S.I. Figure 6. The fit is mostly good for the weaker reflections, whereas strong reflections are fitted poorly, and we speculate that perhaps the misfits arise from incomplete separation of intensities from various twins still present in the data.

The fitted structure has the same layers as the initial guess, although the layers have become somewhat disordered. The in-plane structure is not changed due to the

symmetry of the special sites. A side view of the structure is seen in Figure 13. The structure is seen along the a -axis of the unit cell, and the kagome layers have been shown with black lines. The atomic layers are no longer equidistant, and the structure is more disordered than the initial guess. The hexagonal layers have become significantly buckled, and the Gd atoms have moved closer to the voids in the kagome layers. That also shows as the two neighboring Gd atoms are displaced in opposite directions, just as seen in the Pd_5Ce structure. The Pt atom in the hexagonal layer with the two Gd atoms have moved down very close to the Pt atoms in the kagome layer below, and are unphysically close. A Fourier difference map comparing the measured and calculated electron densities does show that this Pt atom should be higher. Otherwise the rest of the interatomic distances are more reasonable, although varying more than expected. Table 3 sums up the structure with the unit cell and atomic positions of the 12 unique atoms.

The fitted structure is somewhat disordered, and in order to understand atomic displacement in great detail anisotropic Debye-Waller factors were fitted while fixing the atomic positions. With the amount of data

Figure 13: The final stable structure fit is shown, and the grey spheres are Pt and the green spheres are Gd. The structure is seen along the a -axis, and the black lines are placed on the kagome layers as a guide. Some of the layers have been labeled as in Figure 12, and the atoms in the hexagonal layers have been labeled as well. It is seen that the kagome layers are no longer equally spaced, and the hexagonal layers have become strongly buckled. The neighboring Gd atoms have displaced in opposite directions, increasing the interatomic distance, just as seen in the Pd_5Ce structure. The Pt in the same hexagonal layer as the two Gd atoms have moved down, and is unphysically close to the other Pt atoms in the kagome layer below. Otherwise the interatomic distances in the rest of the structure are more reasonable.

available these Debye-Waller factors are not expected to represent physical atomic motion, but rather comparing them with Fourier difference maps they can indicate

Space group	a (α)	b (β)	c (γ)
R3m	5.3309 Å	5.3309 Å	40.358 Å
160	90°	90°	120°
Atom	x	y	z
Gd ₁	0	0	0.0380
Gd ₂	0	0	0.2302
Gd ₃	0	0	0.9250
Pt ₁	0	0	0.1372
Pt ₂	0	0	0.3500
Pt ₃	0	0	0.4542
Pt ₄	0	0	0.5520
Pt ₅	0	0	0.6654
Pt ₆	0	0	0.7642
Pt ₇	0.5039	0.0078	0.9373
Pt ₈	0.4983	0.9967	0.0516
Pt ₉	0.4735	0.9470	0.1857

Table 3: The unit cell parameters and positions of the 12 atomic positions of the final refined structure model. The atomic coordinates are given in relative units to the unit cell.

particular disorder and potential broken symmetry. The anisotropic Debye-Waller factors are sketched in Figure 14, showing an asymmetrical unit cell. It is seen that Pt₁ has a strong disorder along the z -axis, and also that the K_1 layer has a large degree of disorder in-plane, which is shown in Figure 15.

Figure 14: The anisotropic Debye-Waller factors are sketched in the asymmetrical unit cell. The plot is seen along the a -axis of the structure. Interpreting the Debye-Waller factors as a measure of disorder it is seen that some sites show either disorder in the z -direction or in-plane. As an example Pt₁ shows strong disorder in the z -direction only, whereas Pt₇ shows most disorder in the xy -plane.

Figure 15: The anisotropic Debye-Waller factors is sketched for the K_1 kagome type layer. This particular disorder could indicate a broken symmetry in which 1 or 2 of the Pt atoms move closer to the center of the void (in which a Gd atom is seen). Such a symmetry breaking disorder is indicated by the blue and red lines. This might help alleviate the strain within the kagome layer by increasing the Pt-Pt distance, and could also produces a large number of twins.

4. Discussion

In this paper we have studied Gd modified Pt(111) single crystals. Gd has been deposited on a sputter cleaned Pt(111) surface. From the ISS measurements it could be seen that a Pt overlayer forms after annealing the sample to temperatures above 550 °C. By deposition of 200 Å Gd on a sample heated to 800 °C, it was possible to prepare a thick alloy with a stoichiometry close to Pt_5Gd .

The crystal structure of the sample was investigated using LEED and surface sensitive X-ray diffraction. It was seen that the alloy was sometimes rotated by 30° compared to the Pt(111) substrate. Based on the crystal structure it is suggested that the interface between the alloy and the Pt(111) substrate is a kagome layer, since the bulk Pt(111) consists of hexagonal layers. We speculate that the energy of rotated or not rotated strained kagome layer on top of a non-strained Pt(111) layer is very similar. From the LEED pattern, it could be seen that the Gd/Pt(111) sample had formed a 1.90×1.90 structure, corresponding to a 2×2 structure with (5 ± 1) % compressive strain. This is in accordance with powder XRD experiments performed on Pt_5Gd that shows a compressive strain of 4.8 % [14]. CO TPDs have been made to evaluate the reactivity of the sample. The shape of the desorption peak becomes more well-defined after the deposition of a thick Gd layer, indicating that a more well-ordered surface has been created. The shape of the desorption peak bares many similarities to CO TPDs made on Y/Pt(111) [15]. The desorption peak is extremely sharp, indicating strong attractive interactions between the CO molecules

on the surface. It is beyond the scope of this article to understand the origin of interactions that lead to the shape of this desorption peak.

A large downshift in the desorption temperature was observed. The change in the desorption temperature compared to the desorption temperature for the Pt(111) surface is $\Delta T = 200$ °C, see Figure 6. By using the Redheat method the CO desorption energy on the Gd/Pt(111) and Pt(111) surfaces can be evaluated from the desorption temperature [41, 42], see Table 4. These calculations have been made under the assumption that the desorption processes were first order.

The CO desorption peak from the Pt(111) is rather

	T_{max}	$E_{des;CO}$	ΔE_{des}
Gd/Pt(111)	263 K	0.71 eV	0.56 eV
Pt(111)	460 K	1.27 eV	0.00 eV

Table 4: The CO desorption temperature and the corresponding desorption energy from the different surfaces calculated using the Redheat method. ΔE_{des} denotes the change in desorption energy compared to Pt(111).

broad, and for this surface the high energy limit of the desorption peak has been considered since the CO-CO interactions can be neglected in this temperature limit. This decrease in reactivity is expected for Pt surfaces under compressive strain. A compression of the Pt atoms in the surface will result in a downshift in their d-band center which will cause a weakening of the binding energy of the surface [43–45].

The strain seen in the LEED images is in good agreement with the unit cell of the alloy determined by the XRD patterns, and compared to a 2×2 reconstruction the single crystal alloy is compressed by 3.9 % in-plane. Furthermore the XRD experiments also reveal that the c-axis is compressed around 1 % compared to 18 layers of pure Pt. It is counterintuitive that the alloy has a closer packing than pure Pt, considering that Gd atoms are significantly larger than Pt atoms. We expect the real structure to have a number of vacancies to accommodate the compression. However, the location of the vacancies could not be determined, they may contribute to the large number of twins. The X-ray diffraction measurements have revealed that the alloy does not behave like an ideal single crystal. The alloy forms a rather complicated stacking sequence, as evidenced by the large c-axis. Furthermore the crystallites are very small, giving a large number of twins. All the measured diffraction peaks have been analyzed, except the superspots, which are expected to appear because of the small crystallites. However, many similar structures could give rise to twinning

by merohedry. Other potential structures could also have a different c -axis, being either 2, 3, 6, or 9 atomic layers thick which will give rise to diffraction spots that are completely overlapping with the diffraction peaks from the described structure. This could explain why the fitting procedure underestimates certain diffraction peaks. Nonetheless, since most peaks are described fairly well, this structure is dominant in the alloy. The measuring technique using the rocking scans does not provide the most accurate intensities. Although both factor into the poor structure fit, the twinning is most likely more severe than the measurement error.

The strong buckling seen in the hexagonal layers and the inplane rotational disorder, shown in Figure 15, of the proposed structure may be a way of alleviating the in-plane strain, due to the compression discussed above. The key for the in-plane compression observed in this alloy seems to be the structural motif consisting of a kagome layer stabilized by neighboring Gd atoms; the hexagonal layers are buckling to reduce the strain.

5. Conclusion

Different amounts of Gd have been deposited on a clean Pt(111) surface in the attempt to create an alloy. The surface has subsequently been characterized in UHV using XPS, ISS, LEED and CO TPD. The crystal structure has been investigated using synchrotron based XRD.

- A thin layer of Gd was deposited on a Pt(111) surface. An alloy terminated by a Pt overlayer was formed after heating the sample to 550 °C.
- A ~63 nm thick single crystal alloy of Pt₅Gd was prepared by depositing a thick layer of Gd on a Pt(111) single crystal heated to 800 °C.
- XPS was used to determine the stoichiometry to be close to Pt₅Gd, and ISS measurements showed that the alloy was terminated by a single atomic layer of Pt.
- Both LEED images and bulk XRD measurements show an in-plane compression of 4-5 % of the alloy compared to Pt(111). This value is in good agreement with experimental values reported from Pt₅Gd powders and polycrystalline samples [12, 14, 22].
- CO TPD experiments showed that a downshift in the desorption temperature of 200 °C compared to that of pure Pt(111), indicating a decreased reactivity of the Gd/Pt(111).

- The bulk alloy structure had a high degree of twinning by merohedry and a detailed structure determination was difficult, but a slightly distorted structure was found having a hexagonal unit cell with the parameters $a = 5.3309 \pm 0.0008$ Å and $c = 40.358 \pm 0.012$ Å, and a crystal symmetry of R3m (space group 160).
- The key to the compressed structure is the combination of kagome type layers stabilized by larger Gd atoms.
- The decreased binding to CO, as probed by TPD, is consistent with the compressive strain we measure using LEED and XRD [43]. Assuming perfect scaling between the intermediates of oxygen reduction and adsorbed CO, this surface would interact too weakly with OH for optimal activity [17]. However, we do not anticipate that the structure herein is the active phase for oxygen reduction. Gd will dissolve, forming a relaxed pure Pt overlayer with a lower strain value [12]. This alloy is the precursor for the highly active Pt overlayer.

6. Acknowledgement

For funding of this work we gratefully acknowledge The Danish National Research Foundations Center for Individual Nanoparticle Functionality. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. The Danish Ministry of Higher Education and Science is acknowledged for an EliteForsk travel grant making an extended stay at SLAC possible.

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