Pt$_x$Ce$_{1-x}$ Surface Alloys on Pt(111): Structure and Adsorption* 

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A reinvestigation of the alloying behavior between vapor deposited cerium and a Pt(111) substrate has led to a refined understanding of the structural and adsorption properties of Pt$_x$Ce alloy surfaces. Systematic LEED experiments as a function of cerium coverage and annealing temperature enable a clearer correlation between a number of known as well as new surface alloy phases and transitions between them. Coverages of up to 1 ML Ce lead to the formation of a $(2 \times 2)$ LEED pattern. Initial coverages between 1 and 1.5 ML result in the formation of a $(2 \times 2)+(1.98 \times 1.98)\text{R}30^\circ$ structure. More than 2 ML Ce are needed to produce a pure $(1.98 \times 1.98)\text{R}30^\circ$ structure and, finally, more than 3 ML Ce lead to the formation of a $(1.98 \times 1.98)+(1.98 \times 1.98)\text{R}30^\circ$ phase, after annealing to temperature of up to 1000 K. A comparison with the most relevant bulk Pt$_x$Ce laves phases; i.e., Pt$_3$Ce, Pt$_3$Ce and Pt$_2$Ce, suggests a transition from a more “surface alloy like” character of the $(2 \times 2)$ structure to a more “bulk alloy like” character for the $(1.98 \times 1.98)$-structure phases. CO adsorption experiments, using TPD and HREELS, suggest a pure Pt-kagomé surface termination of all the formed Pt$_x$Ce alloy layers on Pt(111).

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I. INTRODUCTION

In the last decade the application of cerium in industry has steadily grown [1, 2]. Cerium based intermetallic systems are promising materials due to their magnetic, catalytic and hydrogen storage properties [3-6]. The interaction between the $f$- and $d$-states of cerium leads to two different bulk phases, a paramagnetic and a diamagnetic one depending on the pressure and temperature [7, 8]. Alloying of cerium with $d$-metals causes a $d$-band shift and a narrowing of the DOS at the Fermi energy for noble metals, e.g. platinum, by hybridization of the Ce states with the Pt $d$-states [9, 10]. Such Pt$_x$Ce alloy phases show a very low activity towards the adsorption of molecules [11] and, as a consequence, a suppressed carbon poisoning, which promises good application possibilities in catalysis. Additionally these alloy phases might serve, due to the magnetic moment of cerium, as good candidates for magnetic layer structures in storage devices.

For the cerium-platinum binary system different bulk alloys, shown in Fig. 1, are well known [12]. Their structures and lattice parameters are listed in Table I.

While with respect to the formation of surface alloys on Pt(111) the Pt$_3$Ce, Pt$_3$Ce and Pt$_2$Ce bulk alloys need to be emphasized. All three alloy phases are of the so called Laves type. These phases are layer structures of alternating pure Pt layers and intermediate layers with varying Ce- and Pt- occupancy. The pure Pt-layers are the specific building blocks of these alloys and are characterized by a $(2 \times 2)$ vacancy structure, a so-called kagomé net.

Studies on the alloying of Ce with Pt(111) were first published in the early 90’s by Tang et al. [13]. XPS and LEED studies showed that intermixing of Ce with Pt starts at 770 K and different LEED pattern were observed depending on the amount of Ce deposited on the surface. Tang et al. as well as Baddeley et al. observed different structures with LEED [13, 14]. While Tang et al. investigated the alloy structures obtained at 770 K, Baddeley et al. annealed Ce films on Pt(111) at 1000 K for 5 min. For small Ce coverages between 1 and 2 ML Tang et al. reported a $(1.94 \times 1.94)$ LEED pattern, while Ce coverages of 2-3 ML led to a $(1.96 \times 1.96)+(1.96 \times 1.96)\text{R}30^\circ$ structure. For Ce coverages above 3.5 ML a mere $(1.96 \times 1.96)$ structure was observed. While Tang et al. assigned these different LEED structures to different alloy compositions, namely the $(1.94 \times 1.94)$ and the $(1.96 \times 1.96)$ structure to Pt$_3$Ce and Pt$_3$Ce, respectively, Baddeley et al. observed with STM five different alloy phases and ascribed this to different rotations of the Pt kagomé lattices or different top layers of pure Pt or Pt$_3$Ce composition. The corresponding LEED pattern were assigned to a $(2 \times 2)$ and $(2 \times 2)+(2 \times 2)\text{R}30^\circ$ structure, respectively, depending on the initial Ce coverage. But up to date there was no investigation over the whole temperature range between

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FIG. 1: Phase diagram of the Pt-Ce bulk alloys (from Ref. [12]).
TABLE I: Pt-Ce alloy phases, lattice parameters and their bulk structure type [12].

| Phase | Lattice param. [Å] | Structure (type) |
|-------|--------------------|------------------|
| $\text{Pt}_3\text{Ce}_7$ | $a = 10.20$, $b = 6.39$ | hex $(\text{Fe}_3\text{Th})$ |
| $\text{Pt}_2\text{Ce}_3$ | $a = 8.98$, $b = 17.08$ | hex $(\text{Er}_2\text{Ni}_3)$ |
| $\text{PtCe}$ | $a = 3.92$, $b = 10.92$, $c = 4.52$ | orth $(\text{CBr})$ |
| $\text{Pt}_4\text{Ce}_3$ | $a = 13.66$, $b = 5.78$ | hex $(\text{Pd}_4\text{Pd}_4)$ |
| $\text{Pt}_2\text{Ce}$ | $a = 7.7$ | cub $(\text{MgCu}_2)$ |
| $\text{Pt}_3\text{Ce}$ | $a = 4.16$ | cub $(\text{Cu}_3\text{Au})$ |
| $\text{Pt}_3\text{Ce}$ | $a = 7.65$ | cub $(\text{Ni}_3\text{Ce})$ |
| $\text{Pt}_5\text{Ce}$ | $a = 5.37$, $b = 9.29$, $c = 2.63$ | orth $(\text{CaCu}_5)$ |
| $\text{Pt}_5\text{Ce}$ | $a = 5.37$, $b = 4.38$ | hex |

300 K and 1000 K, and a coherent determination of the different structures can not be found in the literature yet.

Adsorption experiments on these surfaces are very rare, only one XPS study for CO was published by Vermag in 2006, which shows the low reactivity of the $(2 \times 2)$ alloy phase obtained with small Ce coverage (corresponding to the $(1.94 \times 1.94)$ structure according to Tang et al.) [9].

Our LEED and AES reinvestigation over a wide range of Ce coverages and annealing temperatures of the alloy formation leads to a more detailed understanding of the different observed surface structures. Furthermore, experiments with TPD and HREELS on the adsorption of a number of molecules, such as CO, ethene, benzene and $\text{O}_2$ again show a very low reactivity with no significant differences between all observed alloy phases [11].

II. EXPERIMENTAL

The experiments were performed in an ultrahigh vacuum (UHV) chamber operated at a base pressure of $\sim 10^{-8}$ Pa. The system was equipped with instrumentation for high-resolution electron energy loss spectroscopy (HREELS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and a quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD). For the experiments a disk-shaped Pt(111) sample of 9 mm diameter (MaTeck, Julich) was used, which was mounted between twisted tantalum wires wedged into grooves in the side of the crystal. The cooling was provided by a L-$\text{N}_2$ reservoir, which was directly connected to the sample holder.

Cleaning of the sample was achieved by cycles of $\text{Ar}^+$ ion sputtering (2 keV) at 900 K and short annealing at 1150 K. The cleanliness of the Pt(111) surface was monitored by AES and HREELS.

TPD measurements were made with the QMS in line-of-sight with the sample surface using a linear heating rate of 2 K/s, which was controlled by an Eurotherm 2408 temperature controller. The HREELS spectrometer was run at a resolution of $\sim 5$ meV and a primary energy of 2.4 eV. Spectra were recorded in specular geometry at a scattering angle of 60° off normal. The LEED data were collected by a camera. To characterize the different structures an internal calibration with the Pt(111) $(1 \times 1)$ and the $(2 \times 2)$ Pt$_x$Ce structure as well as the superposition of LEED pattern from coexisting phases helped to find the accurate structure determination. Cerium chips, which were wrapped by a tungsten filament, were used for evaporation of Ce. The different Pt$_x$Ce surface alloys were prepared by evaporating Ce onto the clean Pt(111) surface at 300 K followed by annealing. The amount of the deposited Cerium and the subsequent alloy formation were monitored by AES and LEED. A calibration of the evaporated amount of Ce was made by CO “titration” measurements (Fig. 2).

Different amounts of Ce were adsorbed at 300 K and the AES ratio Ce(83 eV)/Pt(64 eV) was determined. After Ce deposition 10 L of CO were adsorbed at 90 K, and a TPD spectrum was monitored. For the pure Pt(111) surface the characteristic CO desorption signal is positioned at 400 K. The decrease of the signal area with increasing Ce(83 eV)/Pt(64 eV) ratio shows a decrease of the free Pt(111) surface. At AES Ce(83 eV)/Pt(64 eV) ratios higher than 0.45 almost no more CO desorption from bare Pt sites is detected. Therefore an AES ratio of 0.40 is taken here as calibration of one ML of Ce. CO desorp-
III. RESULTS AND DISCUSSION

During the annealing of a Ce film deposited at 300 K significant changes are observed in the AES intensities. With increasing temperature the normalized AES Ce(83 eV)/(Pt(68 eV)) ratio first slowly decreases as shown in Fig. 3 for an initial Ce coverage of 2 ML. Starting at 750 K a strong decrease is visible, which marks the onset of alloying. Above 850 K only a very slow further decrease of the Ce AES signal is observed suggesting an essentially stable surface composition. The starting point of the alloying shifts to higher temperatures with rising initial Ce coverage. Conversely, for smaller Ce coverage in the submonolayer regime it decreases by about 50 K. The strong decrease of the AES ratio around 750 K is accompanied by the formation of the Pt kagomé lattice as top layer as concluded from the TPD and HREELS data for CO adsorption described below. Due to the short mean free path length of Pt(64 eV) and Ce(83 eV) electrons [15] the AES signals originate largely from the top two layers of the surface alloys. Thus, the strong decrease of the Ce(83 eV) signal in Fig. 3 is consistent with a Pt termination layer, whereas the Ce is embedded in deeper layers. The minor decrease of the normalized AES intensity below 750 K, which is accompanied by a vanishing of the (1×1) diffraction spots of the bare Pt(111) surface, suggests a Ce diffusion only into the top Pt layer in agreement with former XPS measurements [13]. A thorough analysis of the LEED pattern after deposition of submonolayer up to 3-4 ML amounts of Ce at 300 K followed by annealing for 5 minutes leads to the phase diagram of surface alloys as shown in Fig. 4. The resulting LEED structures are displayed in Fig. 5(a)-(e).

Even for low initial Ce coverages deposited at 300 K the (1×1) LEED pattern from the Pt(111) surface totally vanishes and only a diffuse LEED pattern is observed. Tang et al. [13] observed via XPS measurements for small Ce coverages below 0.3 ML a trivalent character of Ce suggesting the onset of alloying already at 300 K. Annealing of Ce films with a coverage below 0.5 ML restores the characteristic Pt(111) (1×1) structure (Fig. 5(a)). For higher Ce coverages up to 3-4 ML, however, a closer inspection of the LEED pattern leads to a different interpretation of the observed surface structures compared to the previously published results. This became possible by an accurate study of the alloying behavior and an “inter- nal calibration” particularly in the transition regimes for the different observed structures.

For Ce coverages from 0.5 to 1 ML an ideal (2×2) LEED pattern is observed after annealing onto temperatures between 600 K and 1000 K (Fig. 5(b)). In the Ce coverage regime between 1 and 1.5 ML Ce a superposition of the (2×2) and a (1.98×1.98)R30° structure is observed (Fig. 5(c)), while for coverages from 1.5 to 2.5 ML only the latter is observed after annealing above 800 K (Fig. 5(d)). For Ce coverages above 2.5 ML again the (1.98×1.98) structure, now existing in 2 domains not rotated and 30° rotated, is observed (Fig. 5(e)). Only an internal calibration of the various pattern in the course of an annealing series made it possible to distinguish between these four different structures. The former description of the (2×2)-structure by Tang et al. was mainly based on their XPS data suggesting the formation of a Pt₃Ce alloy for small initial Ce coverages. Assuming the ideal lattice parameter of 7.65 Å (see Table I) led these authors to the proposal of a (1.94×1.94) structure. Also the formerly found (1.96×1.96) and (1.96×1.96)+(1.96×1.96)R30° structures were inferred from the XPS results suggesting a Pt₃Ce composition and using the ideal bulk lattice parameter shown in Table I. Additionally, it has never been addressed before that the formerly suggested
FIG. 5: LEED pattern of the different Pt\textsubscript{x}Ce alloy phases on Pt(111) compared to the pure Pt(111) (1 × 1) structure, primary energy 70 eV: (a) Pt(111) (1 × 1), (b) (2 × 2) surface alloy 0.5-1 ML Ce, (c) (2 × 2)+(1.98 × 1.98)R30° surface + bulk alloy in the 1-2 ML range; (d) (1.98 × 1.98)R30° structure of bulk like alloy, (e) 2 domains of rotated and non rotated (1.98 × 1.98)R30° structure (3-4 ML Ce) and (f) schematic LEED structure of the superimposed (2 × 2)+(1.98 × 1.98)R30° structure with a part of the double diffraction spots.

(1.96 × 1.96) structure, which indeed is a (1.98 × 1.98) structure for a Ce coverage from 1.5-2.5 ML, is rotated by 30° compared to the (1 × 1) structure of the clean Pt(111) surface. A two-domain structure at coverages above 2.5 ML of Ce has been described by Baddeley as (2 × 2)+(2 × 2)R30° structure [14]. We assign the former (1.96 × 1.96)+(1.96 × 1.96)R30° structure to a superposition of the (2 × 2) and the (1.98 × 1.98)R30° structure. The schematic LEED pattern is shown in Fig. 5(f). For this phase the intensity of LEED spots and double diffraction spots varies with the percentage of both components on the surface, i.e. (2 × 2) and (1.98 × 1.98)R30°. The schematic LEED pattern in Fig. 5(f) shows the superposition of these two structures. The red net and the red spots result from the (2 × 2) structure, while the blue net and the blue spots are caused by the (1.98 × 1.98)R30° structure. The dark blue / dark red spots show the first, the light blue / light red spots the second order diffraction spots. In Fig. 5(c) it is obvious that these spots are surrounded by additional spots with hexagonal symmetry. These are caused by double diffraction effects, resulting from a linear combination of the (2 × 2) lattice vectors with those of the (1.98 × 1.98)R30° structure. In the schematic LEED pattern in Fig. 5(f) these spots are marked grey and green, respectively. The corresponding net of these double diffraction spots are also colored grey and green, respectively. The grey spots result from a linear combination of the (1.98 × 1.98)R30° structure (blue spots) with the (2 × 2) (grey), respectively. The green (only shown exemplarily on one (2 × 2) spot (green arrow)) result from the inverse linear combination of the lattice vectors. By comparing one and the same annealing series of the late (2 × 2) structure regime with the early (1.98 × 1.98)R30° structure regime enables an internal calibration and a clear distinction between the (2 × 2)- and (1.98 × 1.98)-structure. An annealing series for an initial Ce coverage of 1 ML is shown in Fig. 6.

After annealing for five minutes to 800 K a well-ordered (2 × 2) structure without any additional spots is observed (Fig. 6(a)). After annealing to higher temperatures (900 K, 1000 K), which corresponds to a vertical transition in the phase diagram of Fig. 4 at 1 ML, additional spots in the 30° direction are observed and the (2 × 2) spots are broadened, as shown in Fig. 6(b) and (c). The new spots in the 30° direction are marked by arrows. These additional spots are assigned to the (1.98 × 1.98)R30° structure. A schematic pattern for this is shown in Fig. 7(d).
Fig. 7: LEED pattern (E = 70eV) of Pt₃Ce surface alloys from an initial Ce coverage of 2.0 ML annealed at various temperatures for 5 min: (a) 800 K, (2 × 2) + (1.98 × 1.98)R30°, (b) 900 K (2 × 2) + (1.98 × 1.98)R30°, (c) 1000 K (1.98 × 1.98)R30° and (d) schematic LEED pattern of the (2 × 2)+(1.98 × 1.98)R30° structure. The blue spots result from the rotated structure, the red spots from the (2 × 2) structure. Second order diffraction pattern are in light red/blue.

The (2 × 2) spots are shown in dark red, the LEED spots of the rotated structure are marked in blue. The light red and light blue colored spots, respectively, are second order spots. The complexity of the LEED pattern shown in Fig. 5(c) is merely a consequence of a superposition of the unrotated (2 × 2) and the rotated (1.98 × 1.98)R30° structure. The surrounding spots in Fig. 5(c) are caused by double diffraction from both of these structures. In the existence regime of this pattern (1-1.5 ML Ce) the LEED intensities vary strongly depending on the annealing temperature and the initial Ce coverage, resulting in different contributions of both sublattices. In turn, in Fig. 7 the phase transition for higher initial Ce coverage of 1.5 ML is shown (vertical transition in Fig. 4 at 1.5 ML).

After annealing at 800 K a superposition of the (2 × 2) and the (1.98 × 1.98)R30° structure is visible (Fig. 7(a)). After annealing at 900 K both structures are more intense (Fig. 7(b)). A determination of the lattice parameters from this structure shows that the two structures have slightly different lattice parameters as illustrated by the schematic LEED pattern shown in Fig. 7(d). The red spots result from the (2 × 2) structure, the blue spots from the (1.98 × 1.98)R30° structure. The Pt unit cell vectors are marked in light grey, double diffraction spots are not shown. For the same lattice parameters of the rotated and unrotated (2 × 2) structure an ideal ring with two spots in every 30° direction would be observed. As it is shown in the schematic LEED pattern the blue spots (marked by a blue arrow) resulting from the (1.98 × 1.98)R30° structure are not on the ideal circle, they are slightly shifted towards the center. For an annealing temperature of 1000 K only the rotated (1.98 × 1.98)R30° structure remains visible. The underlying Pt(111) (1 × 1) structure is not visible yet due to the larger number of Pt-Ce alloy overlayers. As suggested by HREELS and TPD data for CO adsorption a pure Pt termination is present at all these surfaces (see below).

These two examples with 1 ML and 1.5 ML initial Ce coverages suggest, that the transitions in the LEED pattern are caused by a change from a “surface alloy character” to a more “bulk like alloy character” and are not caused by distinctly different Laves type phases (Pt₅Ce, Pt₃Ce or Pt₂Ce). A distinction between those cannot be made by LEED alone because of the very similar lattice parameters given in Table I and the difficulty to distinguish them from separate LEED observations. Ideal bulk truncation of the Pt₅Ce alloy would show a (1.94 × 1.94) structure, for the Pt₃Ce alloy a (1.95 × 1.95) structure and finally for the Pt₂Ce alloy phase a (1.97 × 1.97) structure. For small Ce coverage and only moderate annealing (800 K for 5 minutes) Ce interdiffusion only takes place into the first subsurface layer, while the terminating Pt kagomé lattice maintains the interatomic distance of the initial Pt(111) surface resulting in the (2 × 2) structure. Compared to the bulk Laves type phases the (2 × 2) lattice parameter corresponds to a stretching of 4%-6% depending on the alloy, i.e. Pt₅Ce, Pt₃Ce or Pt₂Ce. In this low coverage regime annealing to 1000 K leads to diffusion of Ce into deeper layers and the growth of thicker alloy islands on Pt(111), resulting in the (1.98 × 1.98)R30° structure. This expansion of the Pt kagomé lattice of this structure, though smaller than in all bulk alloy phases, appears to be best accommodated to the Pt(111) (1 × 1) substrate by a 30° rotation. The (1.98 × 1.98)R30° structure is compressed by 1% compared to the Pt(111) surface and has a 0.7%, 1.3% and 2.1% expanded lattice constant compared to the Pt₂Ce, Pt₃Ce and Pt₅Ce bulk alloys, respectively.

For higher Ce coverages in the range of 1.5-2.5 ML the observed alloy structures are suggested to approach successively the bulk alloy lattice parameter of one of the three Laves type Pt-Ce phases, not distinguishable by LEED but with 30° rotation, while for an even higher Ce coverage above 3 ML no difference in stability of the 30° rotated and an unrotated structure seems to exist.
Fig. 8: Structural models of the different laves type Pt$_5$Ce alloy phases Pt$_5$Ce, Pt$_3$Ce and Pt$_2$Ce from top view and side view. For the top view only the first two layers of kagomé nets are shown (light blue for surface kagomé net, dark blue for bulk kagomé net).

As mentioned in the introduction the so-called Pt kagomé lattice is a hexagonal mesh of Pt atoms, in which $\frac{1}{3}$ of the atoms are missing compared to the pure Pt(111) surface. It is therefore characterized by a $(2 \times 2)$ mesh of vacancies, which are surrounded by six Pt atoms. All of the observed Pt-Ce surface alloys are terminated by this characteristic topmost Pt surface layer (in Fig. 8 light blue). The respective alloy phases differ by the stacking of the Pt kagomé nets (A, B, C in Fig. 8). This stacking can result in the sequences AA, AABB and ABC for Pt$_5$Ce, Pt$_3$Ce and Pt$_2$Ce, respectively. Cerium atoms are always placed above the sixfold Pt hollow sites. For the Pt$_5$Ce and the Pt$_5$Ce alloy phases they are colored light red, for the Pt$_2$Ce phase they are colored dark red. The different alloy compositions are further distinguished by a different number of the threefold hollow sites (marked in red and dark grey in Fig. 8 depending on the filling with Ce or Pt for the different alloys), which are filled with either Pt or Ce atoms. Filling all threefold hollow sites of the kagomé net with Pt atoms leads to one layer of Pt$_2$Ce composition (red layer of Pt and Ce atoms in the Pt$_5$Ce structure in Fig. 8). Filling half of the threefold hollow sites with Pt and the other half with Ce atoms leads to the interlayer structure shown in the model of the Pt$_5$Ce alloy. In this case Ce-Pt-Ce triple-layers are found between two Pt kagomé nets, which are displayed in the corresponding side view. In case of the kagomé net stacking ABC the periodicity is as long as marked by the light grey bar in the side view of the Pt$_2$Ce structure. For the Pt$_5$Ce alloy structure a stacking of the Pt kagomé net followed by one Pt$_2$Ce layer leads to a Pt$_5$Ce composition. The Pt$_5$Ce alloy structure, thus, results from a consecutive stacking of Pt-Pt$_2$Ce bilayers. Finally, the Pt$_3$Ce alloy phase can be thought of as a mixture of Pt$_2$Ce and Pt$_2$Ce structural motifs as marked by the orange bars in Fig. 8 (bottom). The layers between the A and B stacked kagomé nets correspond to the Pt$_2$Ce structure type. In between these two layers the characteristic Ce-Pt-Ce triple layer motive becomes obvious. Hence the Pt$_5$Ce composition is reached by a Pt$_5$Ce bilayer followed by a Ce-Pt-Ce (Pt$_2$Ce) triple layer. Again, the common structural motif of all alloy phases is the same Pt-Kagomé net.

For all structures observed in LEED a pure Pt kagomé lattice termination is suggested, because desorption experiments with ethene, benzene, CO and O$_2$ [11] suggest a very low reactivity of these alloy phases. As an example we present here only HREELS results of adsorbed CO as probe molecule, a full account of the adsorption experiments will be published elsewhere [11]. The analysis of the HREELS spectra of adsorbed CO (Fig. 9) shows, compared to the pure Pt (111) surface, only a slight shift in the characteristic vibrational modes. The loss of features show a more “Pt-like” than a “Ce-like” behavior of CO, suggesting a pure Pt-termination of all alloy surfaces with only minor differences. We can exclude an adsorption of CO in the six fold holes of the surface Pt-kagomé lattice on top of Ce atoms in the next layer, as well as on a Ce terminated surface, because CO adsorption data on Ce films show loss features at 320 cm$^{-1}$ and 2168 cm$^{-1}$ for the Ce–CO and the C–O vibrational modes, respectively (not shown in Fig. 9). Furthermore, on a Ce surface CO is found to decompose into O and C, which leads to typical phonon loss features in HREELS at 346 cm$^{-1}$ resulting from cerium oxide patches. This “cerium like” behavior of CO cannot be observed for all the present alloy systems. Instead, the HREELS investigations of the surface
alloys shown in Fig. 9 clearly favor CO in atop adsorption sites on the surface Pt-kagomé lattice of the Pt$_x$Ce surface alloys.

For CO saturation coverage on Pt(111) the 2095 cm$^{-1}$ loss feature arises from the C–O stretching vibration of CO adsorbed in atop positions, while the loss at 1843 cm$^{-1}$ is assigned to the C–O stretching mode from CO in bridge positions [16]. Furthermore, both of these species can also be distinguished by their loss signals at 461 cm$^{-1}$ and 385 cm$^{-1}$ from the Pt–CO vibrational modes, respectively. In turn, for the Pt$_x$Ce surface alloys only one strong loss feature is observed at 2062-2070 cm$^{-1}$, resulting from the intramolecular C–O stretching vibration. The other dominating loss of features at 397-420 cm$^{-1}$ can also be distinguished by their loss signals at 461 cm$^{-1}$ to 412 cm$^{-1}$. This shift points to a hybridization of the Ce-states with the Pt 5d-states, thereby leading to a weaker Pt–CO bonding on the alloy surfaces than on pure Pt(111).

TABLE II: Comparison of the vibrational modes of CO on Pt(111), Ce and Pt$_x$Ce alloy surfaces.

|                  | Pt(111) top | Pt(111) bridge | Pt$_x$Ce/Pt(111) | 2 ML Ce |
|------------------|-------------|----------------|-----------------|--------|
| Pt–C stretching mode | 461         | 385            | 410             | 329    |
| C–O stretching mode | 2095        | 1843           | 2070            | 2168   |

FIG. 9: HREELS of a saturation coverage of CO on the different Pt$_x$Ce alloy phases compared to the pure Pt(111) surface (bottom spectrum).

loss frequencies is only in the range of 10 cm$^{-1}$ for the different alloy systems. Only for not fully closed surface alloy films with remnant Pt patches the loss signal at 1614 cm$^{-1}$ is found, which can be assigned to CO adsorbed at Pt step edges. In agreement with STM investigations [17] of the alloying behavior, alloy formation begins on the Pt(111) steps and a “rough” remaining Pt surface is obtained. Compared to the CO stretching vibration on pure Pt(111) at 2095 cm$^{-1}$ this vibrational frequency is shifted down only by about 25 cm$^{-1}$ to 2062-2070 cm$^{-1}$ on all alloys. Also the Pt–CO stretching energy is shifted down by about 50 cm$^{-1}$ from 461 cm$^{-1}$ to 412 cm$^{-1}$. This shift points to a hybridization of the Ce-states with the Pt 5d-states, thereby leading to a weaker Pt–CO bonding on the alloy surfaces than on pure Pt(111).

IV. SUMMARY

It was well known that annealing of Ce films deposited on Pt(111) at 300 K leads to well ordered alloy surfaces. By the aid of renewed and improved LEED experiments a new assignment of the observed structures could be made here. The differences in the observed LEED structures are not caused by different genuine phases Pt$_x$Ce, Pt$_x$Ce or Pt$_x$Ce, but are caused by a transition from a “surface alloy-like” character where Ce atoms are situated in the second surface layer to a more “bulk-alloy-like” character, where Ce is also incorporated in deeper layers. While the “surface alloy”, formed by annealing of Ce coverages of up to at most 1 ML, are characterized by a (2 × 2) pattern, annealing of Ce amounts larger than 1 ML (up to 3 ML) results in more “bulk-like” alloys and the appearance of a (1.98 × 1.98)R30° pattern. For initial Ce coverages larger than 3 ML the latter coexists with an (unrotated) (1.98 × 1.98) pattern. A distinction between the (2 × 2) and (1.98 × 1.98) structure was possible here only by the systematic investigation of complete annealing series with different initial Ce coverages. In these series transitions between the (2 × 2) and the (1.98 × 1.98)-structures resulted in superimposed LEED-pattern of both and, thereby, the possibility of an “internal” calibration. Compared to the relevant bulk Pt$_x$Ce laves phases Pt$_x$Ce, Pt$_x$Ce and Pt$_x$Ce the (2 × 2) “surface alloy” is expanded by 4-6%, respectively. In turn, the (1.98 × 1.98)-phases (rotated and unrotated) are only expanded by 1-2%, and are, thus, already more “bulk-like”. TPD and HREELS measurements for CO adsorption on all formed Pt$_x$Ce alloy layers on Pt(111) suggest a pure Pt-kagomé net termination. Even though purely Pt-terminated these alloy films are very unreactive towards molecular adsorbates such as CO, ethene, benzene and O$_2$, as will be described in a forthcoming paper [11].
[1] A. Trovarelli, Catalytic Science Series Vol. 2, *Catalysis by Ceria and Related Materials* (Imperial College Press, London, 2005).

[2] US geological survey Fact Sheet 087-02 (http://pubs.usgs.gov/fs/2002/fs087-02/).

[3] P. A. Dowben, D. La Graffe, and M. Onellion, J. Phys. Condens. Matter 1, 6571 (1989).

[4] C. Schild, A. Wokaunand, and A. Bauker, Surf. Sci. 270, 520 (1992).

[5] J. W. A. Sachtler and G. A. Somorjai, J. Catal. 81, 77 (1983).

[6] J. Rothman, C. Meyer, D. Givord, J. Vogel, M. Finazzi, A. Fontaine, J.-P. Kappler, and N. B. Brookes, Physica B 259-261, 1138 (1999).

[7] I. S. Sandalov, O. Hjortstam, B. Johansson, and O. Eriksson, Phys. Rev. B 51, 13987 (1995).

[8] M. Däne, PhD. Thesis, University of Halle-Wittenber (2008).

[9] B. Vermang, M. Juel, and S. Raaen, Phys. Rev. B 73, 033407 (2006).

[10] B. Hammer and J. K. Nørskov, Adv. Catal. 45, 71 (2000).

[11] J. M. Essen, C. Becker, and K. Wandelt, in preparation.

[12] Landolt-Börnstein, Volume 5c (Springer, Berlin, Heidelberg, New-York, 1993).

[13] J. Tang, J. M. Lawrence, and J. C. Hemminger, Phys Rev. B 48, 15342 (1993).

[14] C. J. Baddeley, A. W. Stephenson, C. Hardacre, M. Tikhov, and R. Lambert, Phys. Rev. B 56, 12589 (1997).

[15] M. P. Seah and W. A. Dench, Surf. Interface Anal. 1, 86 (1979).

[16] H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic Press, New York-London-Paris, 1982) and references therein.

[17] U. Berner and K. Schierbaum, Thin Solid Films 400, 46 (2001).