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Evidence for a cubic-to-icosahedral transition of quasi-free Pd–H-clusters controlled by the hydrogen content

On the phase transitions in Pd–H-clusters

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Abstract. An *in situ* synchrotron radiation study of quasi-free five nanometer-sized palladium clusters during hydrogen absorption is combined with molecular dynamics simulations to investigate the structural development. In the diffraction patterns, strong intensity changes are found that provide evidence for a structural phase transformation that is significantly different from the α–α'–Pd–H bulk phase transition. The structural transition is reversible and driven by the hydrogen concentration. The intensity changes are consistent with a cubic-to-icosahedral structural phase transition obtained in molecular dynamical simulations using embedded-atom-method potentials.

PACS. 64.70.Nd Structural transitions in nanoscale materials – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 68.65.-k Low-dimensional, mesoscopic, and nanoscale systems: structure and nonelectronic properties

Nanometer-sized metal clusters are known to have properties different from bulk samples. As the size of the cluster is reduced, the surface-to-volume fraction becomes large, therefore, the contribution of the surface to the total energy becomes more important. To reduce the total energy, the clusters tend to form a more spherically shaped surface. For the crystalline face centred cubic (fcc) metal clusters, cuboctahedra are found [1,2]. These clusters still show the crystalline symmetry of the large, bulk-like system. Below a critical size, for palladium, gold, silver and other small metal clusters, new structures with icosahedral and dodecahedral symmetry have been reported [3–6].

The study of this structural change between the low-dimensional system and the larger system has recently become a topic of intense experimental research [1,7,8]. The size dependency of the structural change was recently confirmed by Reinhard *et al.* for copper clusters [7]. Rearrangements between icosahedra and cuboctahedra were calculated by Wales and Munro on very small Pd-clusters [9]. Another, size independent structural transition was reported for silver clusters that were prepared at different evaporation temperatures [8]. In both cases, the structural change is measured as a function of constant cluster size and constant temperature of the "as-prepared" clusters and, therefore, the structure stays also constant for the apparent clusters. High resolution electron microscopy studies have shown that the structure of a small cluster can flip between the icosahedral, the cubic and other more complicated structures under the influence of a high voltage electron beam [1,10]. This fluctuation occurs rapidly and is a statistical process that can not be controlled. Up to now, there seems to be no experimental method known where the structural change of the same group of clusters can be controlled by one single parameter.

To study the intrinsic structure of metal clusters, it is important to minimise the interactions between the cluster and the surrounding medium [7]. This can be achieved by stabilising the clusters in surfactant shells. Reetz and co-authors recently described an electrochemical technique to prepare such clusters with a narrow size distribution [11,12]. These clusters remain quasi-free during expansion because the modulus of elasticity of the surfactant shell is orders of magnitudes lower than that of the clusters.

Thermodynamic properties of clusters are visible, especially, in binary (or multi-component) systems with their additional degrees of freedom. Whereas, it is difficult to prepare binary metal-metal clusters over a broad concentration range, hydrogen-metal clusters can be prepared with ease. In the metal-hydrogen system, the high mobility of hydrogen allows alloying the metal with hydrogen even

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at room temperature quickly by using a suitable external partial pressure of hydrogen gas. The external pressure is in equilibrium with the internal hydrogen concentration and, therefore, can be controlled. Furthermore, at the low temperature of 300 K, cluster agglomeration is prevented. At higher temperatures above approximately 400 K, agglomeration effects can not be neglected.

A well-studied binary bulk system is the palladium-hydrogen (Pd–H) system. It shows a single miscibility gap that, at room temperature, is present between α (0.9% H/Pd), and α' (58% H/Pd)[1]. The two phases have fcc-lattice structures. The latter structure is expanded by $0.063{\cdot}c_{\rm H}$ [H/Pd] [13]. Compared to bulk Pd–H, 3 nm quasi-free Pd–H clusters show an extended α-phase solubility limit [14–17]. A phase transformation between the α and α'-like phase occurs [14,17] and the solubility of this α'-like phase is reduced compared to bulk [14]. The pressure plateau of the two-phase region was found in the pressure range expected for bulk metal data [14,18]. Pd clusters are used as a model system in our experiments.

In the present paper we report on a new possibility of a controlled structural transition of small Pd-clusters by adding hydrogen. The experimental results will be interpreted in conjunction with molecular dynamics (MD) simulations. By combining both experimental measurements and MD-simulations, the structures of clusters can be determined.

The clusters were electrochemically prepared by Reetz' technique [11]. They are stabilised by a layer of tetraoctylammonium bromide surrounding the Pd core. Transmission electron microscopy verifies a mean cluster diameter of 5.0 ± 0.7 nm.

The structural changes were measured by *in situ* X-ray diffraction at beam line B2 at the Hamburger synchrotron laboratory HASYLAB at DESY in Hamburg, Germany. The high beam intensity of a synchrotron source is necessary to achieve sufficiently high scattered intensity from the clusters. To reduce the required measuring time per pattern, a focusing toroidal mirror was used. The wavelength of 1.147 Å was selected by a Ge(111) double-crystal monochromator. A high vacuum (HV) gas loading cell with mylar windows was constructed that allows stepwise hydrogen loading between 1 and 1 000 mbar. The equilibrium pressure was controlled with MKS pressure gauges with 0.01% precision. The hydrogen gas purity was 99.9999%, all measurements were performed at room temperature. The diffraction patterns were recorded with constant monitor rates. A NaI scintillation counter with a receiving Soller slit system was used.

Several runs were performed to confirm the characteristic features in the Pd–H cluster diffraction patterns. Each run starts with a pressure of about 10^{-5} mbar. The pressure was increased stepwise up to 1 000 mbar. At each pressure step, diffraction patterns were recorded. For bulk Pd, hydrogen absorption usually expands the lattice and thus shifts the diffraction peaks to lower angles. This was found to be also true for the small clusters. In Figure 1 we have selected two diffraction patterns from the first (1) and the second (2) run. At $2\theta = 29°$ and 34° the characteristic lattice reflections can be seen. They appear at the positions where the Pd–H (111) and (200) reflections are expected. The small peak at $2\theta = 31.5°$ is a background peak as evidenced by a scan taken without clusters. The diffraction patterns indicate an extraordinary behaviour: Above 18.6 (21.3) mbar the intensity of the peak at about $2\theta = 29°$ is significantly reduced. Furthermore, the total integrated intensity between 20 and 45 degrees and the relative intensity between the first and the second peak is reduced. This demonstrates that a structural change takes place during hydrogen absorption, significantly different from a simple lattice expansion and from the known bulk $\alpha - \alpha$' phase transformation. Figure 1 also shows that this structural change is reversible and can be controlled by the hydrogen gas pressure.

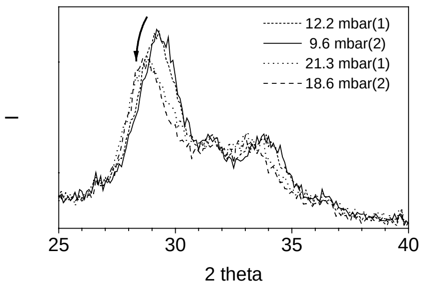

Fig. 1. Diffraction patterns of 5 nm Pd clusters obtained at similar hydrogen equilibrium gas pressures (raw data) during the first (1) and second (2) run. A significant intensity drop of the lower angle reflection occurs between 12.2 (9.6) mbar and 21.3 (18.6) mbar indicating a structural change in the cluster.

So far we considered the raw diffraction data which includes background contributions. After background subtraction the diffraction pattern shows only two pronounced peaks which can be fitted using two Lorentzian profiles. Figure 2 shows the results of fitting: (a) the peak shift of the two Lorentzians, (b) the peak width, (c) the total area in the measured angle range and (d) the relative area between the large (A_1) and the small (A_2) peak, A_1/A_2. At low concentrations a slight shift in both peak positions can be seen. This can be attributed to a lattice expansion caused by hydrogen absorption. Between 12 mbar and 17 mbar hydrogen gas pressure, a pronounced peak shift appears. This might be correlated with passing through a two-phase region, because the overlapping of each pair of reflections results in peak broadening (*cf.* Fig. 2b), and a larger mean peak position shift. At higher pressures, outside the two-phase region, only one single phase exists and the broadening should vanish. This appears to be the case of the lower angle reflection peak. It is not observed for the reflection peak at a higher angle where the original width is not retained. The difference is marked by an arrow. Figure 2c gives the integrated intensity between 25 and 45 degrees. It drops between 17 mbar and 18 mbar to 85% of its initial value. This also is not consistent with the phase separation known from bulk Pd–H.

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[1] The concentration $c_{\rm H}$ of the interstitial alloy is given in number of hydrogen atoms per Pd atom H/Pd or, equivalently, per number of interstitial octahedral lattice sites.

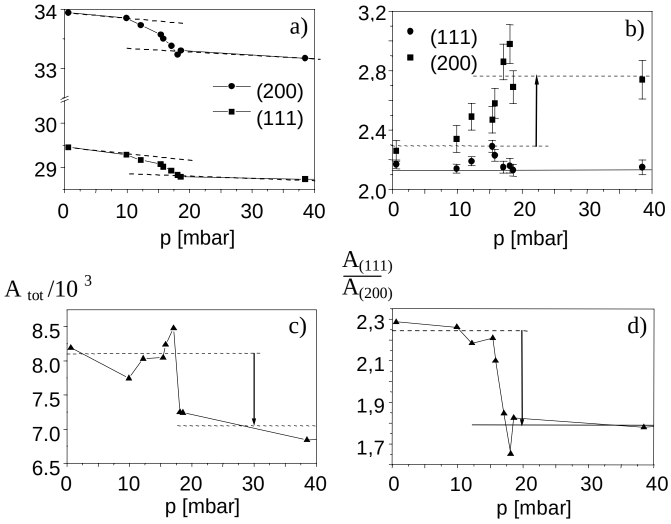

Fig. 2. Results of two Lorentzians that fit the diffraction patterns after background substraction. The peak shift of the two Lorentzians is shown in (a) and the peak width δ in (b). Part (c) shows the total area A_{tot} and in (d) the relative area between the low angle and the high angle reflection, A_1/A_2, is plotted as a function of the hydrogen gas pressure.

Figure 2d demonstrates the sudden decrease in the integrated intensity of the low angle reflection compared to the higher angle reflection. This gives a third hint to structural changes above 18 mbar. To summarise the experimental results, three indications for additional structural change were observed: (i) the drop in the integrated intensity between 25 and 45 degrees, (ii) the decrease in the relative integrated intensity of the two diffraction peaks and, (iii) the different peak broadening behaviour.

As pointed out by Kaszkur [19] diffraction analysis of small clusters is beyond the Bragg law. Therefore, simulations are necessary to determine the diffraction pattern of nano-particles. To elucidate the structure of small Pd clusters, molecular dynamics (MD) simulations were performed using the modified embedded atom method (MEAM) potentials for Pd [20]. The MEAM potentials adequately reproduce the lattice parameter, the thermal expansion and the elastic modulus for the bulk metal. They further describe the phonon spectra, the structure of liquid metals, the dislocation properties and the fracture properties with good accuracy [20]. Additionally, they give a realistic description of the metallic cohesion [20]. Since structural transitions in clusters are strongly affected by the mechanical properties we choose these potentials. With the MD simulations technique, the atomic structure is allowed to relax from an initial starting configuration in an appropriate self-consistent force field. The total energy of the cluster is calculated after each simulation step, usually done at constant temperature and zero pressure. For the simulations the program DYNAMO of Foiles and Baskes were used [21].

A 2 057-atom cuboctahedral (fcc) cluster was relaxed at 1 000 K. The initial cluster relaxes in two picoseconds into a meta-stable equilibrium cuboctahedral structure and then transforms into the icosahedral structure. This structure remains stable more than 100 ps. After further relaxation at 300 K, it has an energy of 1 meV/atom below that of the cuboctahedral structure. The stability of the resulting structure was tested by using different initial structures, cluster sizes and annealing temperatures[2]. Up to the here mentioned size of 2 057 atoms the initial cubic structures all turned into the lower energy icosahedral configuration provided a sufficient combination of temperature and annealing time was used. This demonstrates that the icosahedral structure is energetically more favourable than the cubic structure. We note, that simulations on Pd-clusters published by Kaszkur [19] performed with semi-empirical N-body Sutton-Chen potentials result in different structures. Kaszkur [19] considers the formation of clusters from the melt and model quenched-in thermal-like disorder. This procedure indicates the formation of dislocation- and grain-boundary-carrying cubic structures during the solidifaction process, where annealing of these defects and a further equilibration of the quenched-in structures could not be seen within the time accessible to the proceeding simulation treatment. It should be mentioned that the diffraction pattern obtained by this method can not explain our experimental X-ray diffraction details of the transformed cluster. It also makes difficulties to understand a high concentration of defects in such a small cluster, generated and annealed just by adding and removing hydrogen atoms.

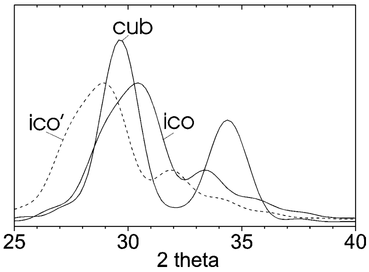

Fig. 3. Calculated diffraction patterns from MD-simulated structures of a 2 057 Pd-atoms containing Pd-cluster. The solid curves are for the cuboctahedron ("cub") and icosahedron ("ico") whereas the broken line originates from the pattern of the icosahedron that is shifted to account for the hydrogen lattice expansion.

From the simulated relaxed structure of the 2 057 Pd-cluster the diffraction intensity $I(k)$ was calculated by fourier transformation. This yields broad reflections corresponding to the small cluster size, as shown in Figure 3. The diffraction pattern of the cuboctahedral structure, plotted with a solid line ("cub"), shows the (111) reflection at about $2\theta = 29.6°$ with large integrated intensity and the (200) reflection at $2\theta = 34.4°$ with smaller integrated intensity. In comparison, the pattern of the icosahedral structure (plotted as a solid line "ico") reveals a low-angle reflection whose position is quite close to that of the (111) reflection of the cubic structure. The maximum intensity is

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[2] N. Jisrawi, A. Pundt, M. Guerdane and H. Teichler, work in preparation.

significantly smaller compared to the cuboctahedral (111) reflection. The maximum intensity drop measured at the lower angle reflection therefore could be interpreted with a structural transformation from the cuboctahedral into the icosahedral structure.

Also, in the vicinity of the (200) reflection of the cubic structure, a reflection peak of the icosahedron is found. Its peak is much larger than the (200) reflection. This is also in good agreement with the measurements. But the intensity of the peak decreased compared to that of the (200) reflection of the cuboctahedron. Furthermore, the peak width of the (111) reflection is larger for the icosahedron than for the cuboctahedron. However, by comparing the measured peak intensity of the (200) and the (111) with that of the ideal cuboctahedron, the measured (200) already appears too small. This might be due to a non-ideal starting morphology which also might explain the changed width of the (111) reflection. Integration of the calculated patterns between 20 and 45 degrees give a slightly smaller total integrated intensity for the cuboctahedral structure pattern as opposed to the icosahedral one. This, furthermore, is in agreement with the experimental results. Therefore, most experimental observations can be explained by a structural transformation from a cuboctahedral into an icosahedral cluster.

The solid curves in Figure 3 show the diffraction pattern of the Pd clusters without hydrogen. Hydrogen absorption leads to a lattice dilatation that shifts the peak positions about 1.5° to lower angles. In the given interpretation, we relate the icosahedral structure to the hydrogen containing structure, resulting in the pattern plotted with the broken line ("ico"). This gives a peak order that is in good agreement with the experimental data.

We re emphasize that the experimentally observed structural change can not be explained with the Pd–H bulk phase transition between the α- and α'-phase. Because of its reversible character and a negligible Pd-diffusivity, morphology changes of the Pd-clusters can also be excluded. In contrast, the proposed structural transition is just an atomic rearrangement and is, therefore, the most probable. We note that there is a lack of simulations of "hydrogen containing clusters" up to now. The slight differences between the measured and calculated pattern are attributed to the fact that, firstly, the starting morphology of the clusters is not ideally cuboctahedral. According to Cleveland *et al.* [23] the most probable morphology is that of a truncated Marks-decahedron. Secondly, the differences are attributed to the addition of hydrogen that also influences the calculated diffraction pattern of the icosahedron.

Within the framework of our interpretation the 5 nm Pd-clusters have cuboctahedral structure which transforms for large hydrogen concentrations into the icosahedral structure, *i.e.* the icosahedral structure is stabilised by hydrogen. The strong influence of hydrogen on a phase transition was already shown by Grönbeck *et al.* by demonstrating that hydrogen reduces the melting temperature of Pd-clusters [24]. Our results demonstrate that, by adding hydrogen, the critical size for the transformation between the low-dimensional icosahedral structure and the crystalline "bulk-like" structure can be shifted to larger dimension. We assume that this appears because hydrogen can occupy outer stretched sites that usually destabilise the icosahedron. By occupying these sites hydrogen relieves strain and allows palladium atoms to lie away from their most favourable hydrogen-free positions. Recent MD-simulations show that hydrogen addition enhances the shearing transition between the cuboctahedron and the icosahedron[3]. Also, this is in good agreement with the reported experimental results.

Coming back to the pressure-composition isotherm discussed at the beginning of this paper, the reduced solubility in the so-called α' now can be interpreted with the new two-phase equilibrium in the case of 5 nm clusters. It is not, as assumed before [14,17,16], the known α-α' two-phase equilibrium of the bulk Pd–H system. It occurs between the cuboctahedral phase and an icosahedral phase labeled IC. Since the α-IC phase transformation occurs in the same pressure range or chemical potential, as the α–α' transformation in the bulk, the difference between the Free Enthalpy of the IC-phase and that of the α'-phase can not be large. This is in good agreement with the calculated small energy difference between the two structures.

To summarise, a hydrogen controlled structural change of 5 nm sized Pd-clusters was found. By combining results of experimental diffraction with MD-simulations the structure was studied. It was deduced that hydrogen-free clusters are stable in the cubic structure and transform into an icosahedral structure after absorbing a certain amount of hydrogen. This suggests that the critical size for the icosahedral-to-cubic structural transition of small clusters can be shifted by hydrogen absorption. The hydrogen-controlled phase transition is reversible for the considered clusters: the structure can be switched between icosahedral and cubic structure by increasing or lowering the hydrogen gas pressure, *i.e.* the hydrogen concentration. Such a reversible and controlled structural phase switching has not been observed before. For the first time, this enables us to study the fascinating phase transition between the icosahedral structure of the low-dimensional system and the crystalline structure of the more bulk-like system in detail. Further studies of this reversible and controlled change between the low-dimensional structure and the bulk-like structure under modified conditions may lead to a deeper understanding of the basic physical properties of small size materials.

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[3] N. Jisrawi, unpublished

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