

## Hydrogen and Pd-clusters

A. Pundt<sup>a,\*</sup>, M. Suleiman<sup>a</sup>, C. Bähitz<sup>b</sup>, M.T. Reetz<sup>c</sup>, R. Kirchheim<sup>a</sup>, N.M. Jisrawi<sup>d</sup>

<sup>a</sup> *Institute of Material Physics, University of Göttingen, Hospitalstrasse 3-7, D-37077 Göttingen, Germany*

<sup>b</sup> *Institute of Materials Science, Darmstadt University of Technology, D-64287 Darmstadt, Germany*

<sup>c</sup> *Max-Planck-Institut für Kohlenforschung, D-45470 Mülheim, Germany*

<sup>d</sup> *Department of Physics, Birzeit University, PO Box 14, Birzeit, Palestine*

### Abstract

Isotherms of Pd–H clusters with different sizes differ from bulk isotherms: they show a largely enhanced solubility in the low-concentration regime. The isotherms resemble those of bulk above the critical point, they show no flat plateau region, but a slope. However, the existence of a hysteresis gives evidence for a phase transition even in small Pd–H clusters. Structural studies of 6.0 nm clusters show a transition between two cubic phases. 3.8 nm Pd–H clusters always show an icosahedral structure in the low and high concentration regime. For an intermediate size of 5.0 nm Pd–H clusters, the lattice structure changes during H-absorption, from cubic to, most probably, icosahedral. The slope in the cluster isotherm's two-phase region is here attributed to stress emerging between the surfactant shell and the cluster during hydrogen-loading. © 2003 Elsevier B.V. All rights reserved.

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### 1. Introduction

To study differences in the physical behaviour between a large size (bulk) and a small size (cluster) system the palladium–hydrogen system is ideal. The bulk behaviour is well studied and many physical parameters are known [1,2]. Because of the noble character of palladium, clusters can be prepared with only a very thin oxide surface that can be removed by a hydrogenation treatment [3]. So, the properties of pure metal–hydrogen clusters can be deduced and compared with those of the bulk metal–hydrogen system.

However, clusters have to be stabilised to prevent undesired agglomeration and growth. This can be done by depositing clusters onto a substrate or by embedding them in a metal or polymer matrix, or in a surfactant shell. Unfortunately, stabilisers effect the physical properties of the clusters. To minimise the stabiliser impact we choose elastically soft stabilisers like polymers or surfactants for our studies [3,4]. Also, chemical effects are expected to be minimised by the comparably weak bonding between the metal and the alkyl chains of the stabilisers. Since soft stabilisers can be

destroyed at temperatures around 100 °C, studies are limited to a small temperature window.

If the hydrogen permeability through a polymer is small, the time-scale for such studies can be very long [3]. Therefore, we will focus on results obtained by using surfactant stabilised clusters. These clusters are directly reachable for the gas molecules which just have to penetrate the surfactant shell. Gravimetric measurements show that thermodynamical equilibrium is reached within 30 min in the single phase regions.

Recently, Reetz and Helbig [5] proposed a method to prepare clusters by an electrochemical technique where the medium cluster size can be controlled by changing the preparation parameters and the cluster size distribution is narrow. This is essential for our purpose to study the influence of the cluster size on the physical properties.

Clusters have a high surface-to-volume atom ratio. Therefore, it is expected that physical properties are dominated by surface effects. Christmann [6] and Behm et al. [7] showed, by studying hydrogen sorption at surfaces of freshly cut palladium bulk material, that these surfaces have a higher solubility compared to bulk. At room temperature, bulk palladium absorbs about 0.6 hydrogen per palladium atom (H/Pd), the palladium surface sorbs about 1 H/Pd and the sub-surface sorbs hydrogen with an increased solubility. Muschiol et al. [8] even found that this sub-surface region

\* Corresponding author. Tel.: +49-551-39-5007;

fax: +49-551-39-5012.

E-mail address: apundt@ump.gwdg.de (A. Pundt).

can be several monolayers deep. Thus, in the palladium surface region an increased solubility is found. This is also expected for surfaces of small clusters. Furthermore, edges and corner sites are available in clusters that additionally increase the cluster solubility compared to bulk. In extremely small clusters of less than 1 nm hydrogen to metal-atom ratios of 8 were reported [9]. From these results, it is expected that the border-phase solubility of clusters will be increased compared to bulk.

With regard to theoretical calculations from Wolf et al. and Lee et al. [10,11] it is proposed that a phase transition is not possible for small clusters any more. This is also expected because of finite-size effects: the critical point, that closes the miscibility gap, is expected to shift to lower temperatures.

In the following, our experimental results on clusters of different medium sizes will be summarised. We will focus on isotherms, taken at room temperature, during hydrogen loading and unloading and structural studies. Comparing both isotherms and structural results the questions whether a phase transition occurs or not will be discussed.

## 2. Experimental details

Palladium clusters were stabilised in tetraoctylammonium bromide by using the electrochemical method described by Reetz and Helbig [5] in which an electrolysis cell with two electrodes is used. By applying a constant current density the Pd-electrode dissolves and single-sized Pd-clusters embedded in the surfactant shell were formed [12,13]. Elemental analyses reveal an amount of 60–80 wt.% of palladium within the cluster-stabiliser mixture. The cluster size and cluster size distribution was determined by transmission electron microscopy and high resolution electron microscopy. The clusters in this paper have sizes between 3.0 and 6.0 nm. All sizes were determined from electron microscopy images by measuring more than 150 clusters. The full width half maximum of each cluster size distribution is about 0.8 nm, and thus, quite narrow. Isotherms were taken by using a gas-loading gravimetric Sartorius micro-balance. The amount of 200–500 mg clusters powder stick to a 100 mm × 20 mm polymer carrier lead, during hydrogen absorption or desorption, to a weight change in the mg-range. Structural studies were performed at the Hamburger synchrotron laboratory HASYLAB at beam line B2. A high vacuum gas-loading cell in transmission geometry was used, the sample was stack onto a polymer carrier (since the measurements were taken in different sessions the beam wavelength differs slightly resulting in different peak positions. To overcome this problem, we marked the positions of the palladium bulk Bragg reflections in every graph). The wavelength was selected by a Ge(111) double-crystal monochromator. Gas loading was performed stepwise and controlled between  $10^2$  and  $10^5$  Pa. Each loading cycle started at a pressure of  $10^{-3}$  Pa. The pressure was monitored by using MKS pressure gauges with 0.01% pre-

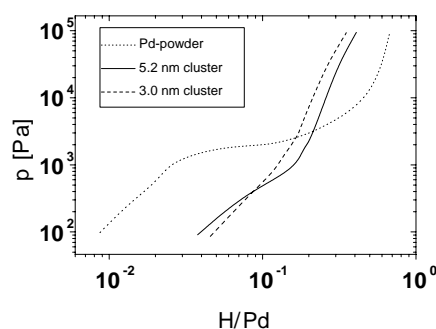


Fig. 1. Isotherms of 5.2 and 3.0 nm palladium–hydrogen clusters in logarithmic scaling [14]. For comparison the palladium–hydrogen bulk isotherm is also plotted. The clusters isotherms resemble those of the palladium–hydrogen bulk system above the critical point: they show an enhanced low-concentration solubility as well as a reduced high concentration solubility. Furthermore, in the medium concentration range the isotherm does not show a plateau but a sloped isotherm.

cision. The purity of the hydrogen gas was 99.9999%, all measurements were taken at room temperature. All samples were pre-treated with hydrogen to remove any oxide layer.

## 3. Isotherms and structural studies on palladium–hydrogen clusters

Gravimetric measurements were obtained by monitoring the hydrogen sorption behaviour of the palladium clusters. Fig. 1 summarises the isotherms of 5.2 and 3.0 nm palladium–hydrogen clusters in logarithmic scaling. For comparison the palladium–hydrogen bulk isotherm is also plotted. The clusters isotherms resemble those of the palladium–hydrogen bulk system above the critical point: they show an enhanced low-concentration solubility as well as a reduced high concentration solubility. Furthermore, in the middle-concentration range the isotherm does not show a flat plateau but a slope. This finding supports the occurrence of a reduced critical point. However, by adding the cluster desorption isotherm, one finds a hysteresis. This is shown in Fig. 2a) for 5.2 nm clusters where the sorption (black cycles and triangles) and the desorption curve (white cycles) does not match in the pressure range between  $2 \times 10^2$  and  $10^3$  Pa and a hysteresis opens. Usually, a hysteresis is not observed above the critical point. If the hysteresis is taken as a fingerprint of a phase transition and a two-phase field, the cluster's critical point is still above room temperature.

The clusters 'sloped plateau' appears at those pressures where the bulk isotherm also shows its plateau for the  $\alpha$ - $\alpha'$ -phase transition. This gives evidence for a bulk-like phase transition between two cubic phases also for clusters.

To clarify the questions, if there appear bulk-like phases during hydrogen loading also in small clusters and if there is a phase transition, X-ray diffraction pattern were recorded. For 6.0 nm clusters, cubic Bragg reflections were measured, as shown in Fig. 3. During hydrogen loading (increased hy-

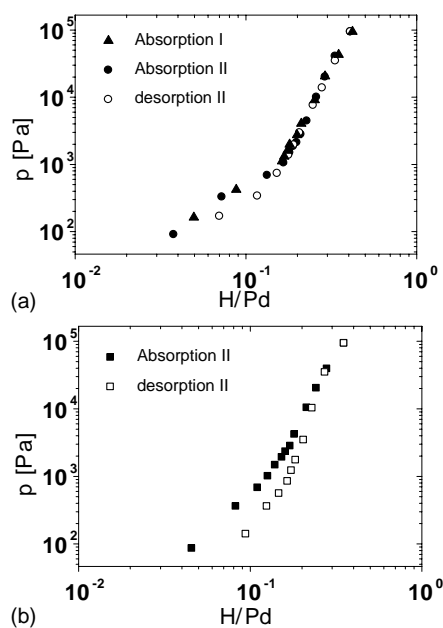


Fig. 2. Pressure–concentration isotherms of (a) 5.2 nm Pd–H clusters and (b) 3.0 nm Pd–H clusters obtained by gravimetric measurements at room temperature during loading and unloading [14]. A hysteresis can be seen opening in the medium concentration range.

drogen gas pressure) the reflections shift to smaller angles. This is due to the lattice expansion during hydrogen absorption in interstitial lattice sites. At  $6.5 \times 10^2$  Pa, a new set of reflections is visible also belonging to a cubic phase, but with a larger lattice parameter. These reflections are comparable to those of the cubic bulk  $\alpha'$ -phase whereas the lattice parameter is smaller than that of the bulk system. This

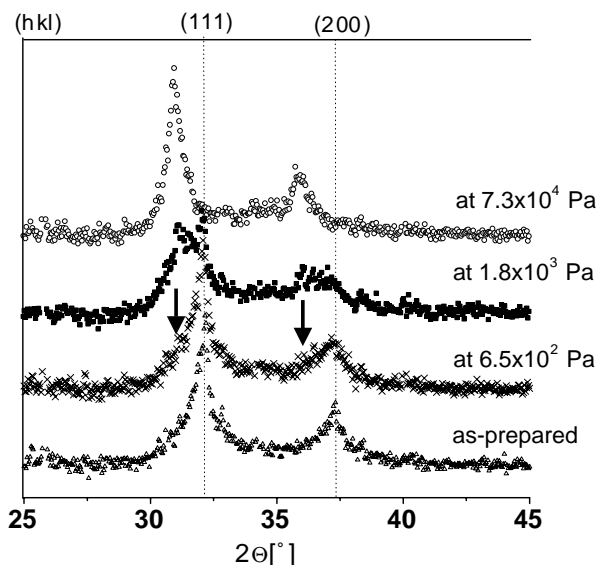


Fig. 3. Four X-ray diffraction pattern of 6.0 nm Pd–H clusters for different H-gas-pressures. Cubic lattice reflections were measured. A phase transition is visible for pressures at about  $6.5 \times 10^2$  Pa (new reflections marked with arrows) [14].

supports the existence of bulk-like phases in 6.0 nm Pd–H clusters. Their lattice parameter is slightly changed. Also it verifies the phase transition in 6.0 nm small clusters. At pressures above  $3 \times 10^3$  Pa, only the reflections of the hydride phase are visible, showing that the transition is completed.

Surprisingly, the two sets of reflections appear together at the same equilibrium pressure. With increasing equilibrium pressure the total integrated intensity of the first set decreases and the second ones grows.

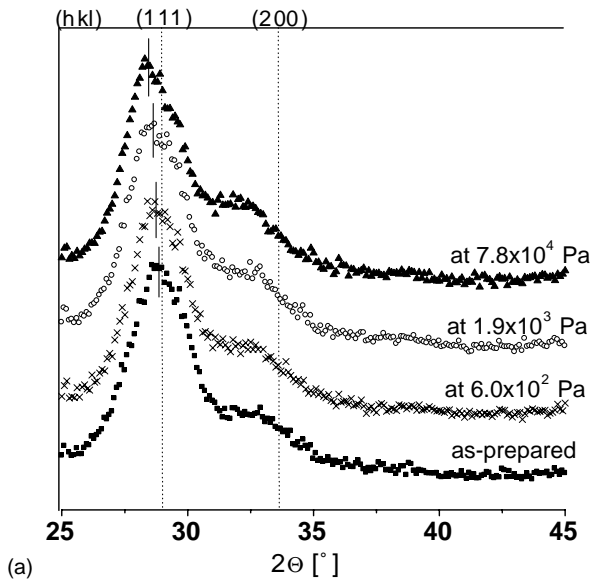
This is a big difference to the bulk phase transition, where a higher equilibrium pressure results in the appearance of the  $\alpha'$ -phase and a complete vanish of the  $\alpha$ -phase lattice reflections. This is due to a constant chemical potential, or a constant equilibrium pressure, during the phase transition. But in clusters the two phases appear simultaneously. This is in good accordance with the isotherm where the hysteresis was also found in a concentration range with a sloped isotherm. Also, it strongly shows that the critical point for the phase transition is still above room temperature for the 6.0 nm clusters.

Fig. 1 also shows a ‘sloped plateau’ for the 3.0 nm small Pd–H clusters. Again, it appears in the same pressure range as that of the Pd–H bulk system. A hysteresis is also found for these small clusters (Fig. 2b) verifying the existence of a phase transition. But the diffraction pattern of (a) 3.6 nm and (b) 3.0 nm clusters in Fig. 4 show some differences. Each peak of the pattern is extremely broad, as expected for small particles like clusters. Additionally, the position of the first and the second reflection at lower angle are narrowed compared to the (1 1 1) and (2 0 0) cubic lattice reflections. And, there is an increased intensity between 50 and 55° (not shown here), showing the presence of structures other than the cubic ones.

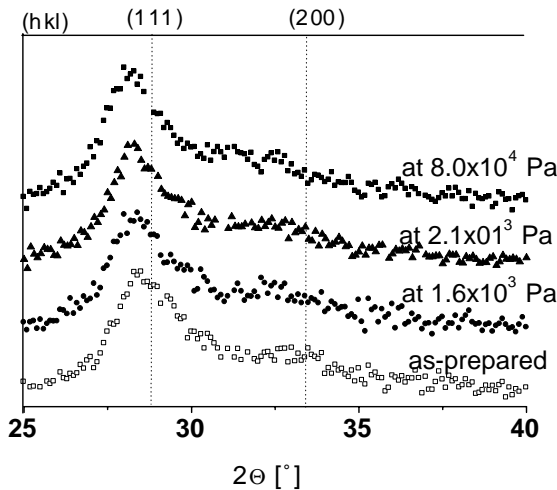
HREM images show an amorphous-like picture of these small clusters. No straight lattice fringes can be found. In the HREM diffraction modus, for some clusters five-fold symmetries can be determined. This gives evidence that for these clusters non-translational structures appear. Results on Au-, Pd- or Cu-clusters [15–17] show that these structures can be icosahedral as well as decahedral and others.

According to molecular-dynamics simulations on palladium clusters with closed atomic shells [18,19] the icosahedral structure is energetically favoured compared to the cubic structure for small sizes. Decahedral structures or others were never gained during these simulations. Therefore, we suppose that small palladium clusters have icosahedral structure.

Hydrogen absorption shifts the Bragg reflections to smaller angles which is, again, due to the lattice expansion during hydrogen absorption in interstitial lattice sites. In the measured pressure range only a shift can be seen, no additional set of reflections is visible. But, for the broad reflections strong peak overlapping can occur and new reflections can be difficult to detect. To test, if strong overlapping of two sets of diffraction pattern in a certain pressure range occurs, we checked the peak width of the lower angle



(a)



(b)

Fig. 4. X-ray diffraction pattern of (a) 3.6 nm and (b) 3.0 nm Pd–H clusters for different H-gas-pressures [14]. Each peak is very broad due to the small cluster size. The positions of the two lower angle reflections are narrower compared to those of the cubic lattice.

lattice reflection over the whole measured pressure range. No additional peak broadening could be found within the experimental error. Nevertheless, because of the occurrence of hysteresis, we conclude that a phase transition occurs. For the small clusters, we assume that it occurs between icosahedral phases [14].

Even more interesting is the case of intermediate sizes. One example is 5.0 nm Pd–H clusters whose X-ray diffraction pattern, for  $1.2 \times 10^3$  and  $2.1 \times 10^3$  Pa, are shown in Fig. 5. While at low pressures only a shift in the lattice reflections intensity appears around  $1.8 \times 10^3$  Pa. The integrated intensity of lower angle reflection shrinks while the reflection beside stays constant in its integrated intensity. This can be interpreted by a lattice change, from the cubic lat-

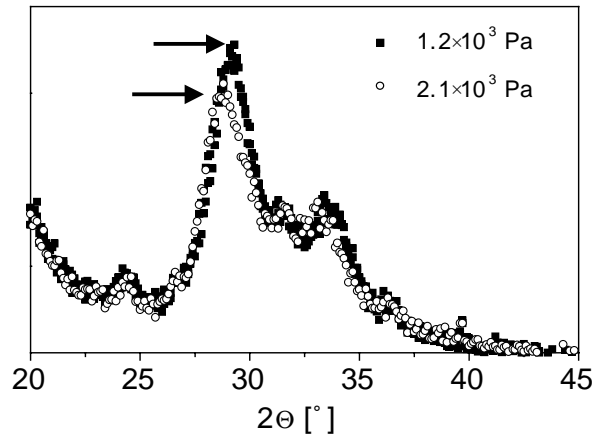


Fig. 5. X-ray diffraction pattern of 5.0 nm Pd–H clusters for two different H-gas-pressures [18]. At  $2.1 \times 10^3$  Pa, the pattern changes its shape. While the second reflection stays constant in its integrated intensity, the first one's intensity is reduced (arrows).

tice to, most probably, an icosahedral structure [18]. This lattice change is found to be reversible, during unloading the original lattice reflection intensities reappear. In a second loading-unloading cycle the pattern showed exactly the same intensity change.

#### 4. Discussion

The isotherms of Pd–H clusters resemble those of Pd–H bulk above the critical point. As discussed above, this is not because of a reduced critical point. We assume that different contributions lead to the unusual isotherms shape.

The isotherms of clusters show an enhanced solubility in the low concentration range compared to bulk, and a reduced one in the high concentration range. We attribute this to additional sorption of hydrogen in subsurface sites (the surface is assumed to be covered by hydrogen mono layer at room temperature). At low concentration this additional sorption shifts the isotherm to larger concentrations. At high concentrations, these sites do not participate in the hydride formation which results in a reduced measured concentration as long as the medium concentration in the additional sorption sites is below that of the hydride [3,4].

Phase transitions were found in all Pd–H clusters, by looking at the lattice structure or, in case of small clusters, by measuring a hysteresis. In bulk Pd–H the hysteresis was understood as resulting from dislocations generation and movement during the phase transition [20,21]. However, in small clusters dislocations will not occur and the hysteresis in cluster isotherms must have a different origin. Schwarz and Katchaturian [22] have proposed another explanation for the hysteresis in Pd–H by applying the thermodynamics of an open, coherent system [23]. This thermodynamics differs drastically from the classical, Gibbsian thermodynamics. By taking coherency stress into account different

chemical potentials can be achieved. Schwarz and Katcharian showed that this leads to different chemical potentials during loading and unloading in Pd–H, thus, forming a hysteresis loop. Following this theory, a relation between the absorption and desorption pressure has to be fulfilled. Sachs et al. [3] showed that this relation holds for different Pd–H cluster isotherms. To conclude, hysteresis in clusters can be understood by means of the thermodynamics of the open, coherent system. In this thermodynamic approach, the small sample size was not taken into account.

Now the question arises, why the measured isotherms show a ‘sloped plateau’ and not a flat one. In the beginning, we argued to choose mechanically soft stabilisers like surfactants or polymers. However, as recent results on thin film deposited on polymer substrates have shown, also here large stresses can arise during hydrogen loading [24]. In case of a niobium film on polycarbonate compressive stress of about –2 GPa were calculated. But, as long as the polymer substrate is thin, it can be strained and the total stress is reduced. However, mechanical stress gives an additional contribution to the chemical potential [25,26] and, therewith, tilt the plateau into a ‘sloped plateau’. This was argued to happen for thin metal–hydrogen films deposited on elastically hard substrates [25,26]. We assume that stress also arises between the cluster and its surfactants and that this stress tilts the plateau into a ‘sloped plateau’. Other explanations, like a broad cluster size distribution and a variety of bend surface energy contributions [27] can be excluded because, in our experiments, the cluster size distribution is narrow but the ‘sloped plateau’ is visible. Comparing our results with those obtained by Züttel et al. [28] on clusters compressed in a copper matrix shows that for their clusters, also, a ‘sloped plateau’ exists. The slope is steeper than for our clusters. This finding is in accordance with the assumption that stress changes the clusters isotherms: it is expected that the stress arising between palladium and a metal is larger than that arising between palladium and a surfactant shell. To conclude, the cluster isotherm shape can be explained by taking subsurface sites as well as mechanical stress into account.

## 5. Summary

Isotherms of Pd–H clusters differ drastically from those of the Pd–H bulk system. They resemble isotherms above the critical point for the phase transition: they show an increased solubility in the low concentration range, a decreased solubility in the high concentration range and, in between, a sloped isotherm. Changes in the solubility were attributed to hydrogen sorption in subsurface sites. Measurements of hysteresis have shown that phase transitions must occur in clusters even though the isotherms show no flat plateau region. Structural studies on large clusters have directly monitored the phase transition by the appearance of cubic hydride reflections. For small clusters only reflection shifts could be

detected during hydrogen loading. For 5.0 nm clusters, a reversible lattice change occurs during hydrogen loading between a cubic and, most probably, an icosahedral structure. The ‘sloped plateau’ of clusters was attributed to mechanical stress occurring between the Pd-cluster and its surfactants during hydrogen sorption.

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## References

- [1] G. Alefeld, J. Völkl (Eds.), *Hydrogen in Metals I*, Bd 28 Topics in Applied Physics, Springer, Berlin/Heidelberg/New York, 1978.
- [2] G. Alefeld, J. Völkl (Eds.), *Hydrogen in Metals II*, Bd 29 Topics in Applied Physics, Springer, Berlin/Heidelberg/New York, 1978.
- [3] C. Sachs, A. Pundt, R. Kirchheim, M. Winter, M.T. Reetz, D. Fritsch, *Phys. Rev. B* 64 (2001) 075408.
- [4] A. Pundt, C. Sachs, M. Winter, M.T. Reetz, D. Fritsch, R. Kirchheim, *J. Alloys Comp.* 293–295 (1999) 480.
- [5] M.T. Reetz, W. Helbig, *J. Am. Chem. Soc.* 116 (1994) 7401.
- [6] K. Christmann, *Interaction of Hydrogen with Solid Surfaces*, Elsevier, 1988.
- [7] R.J. Behm, V. Penka, M.G. Cattania, K. Christmann, G. Ertl, *J. Chem. Phys.* 78 (1983) 7486.
- [8] U. Muschiol, P.K. Schmidt, K. Christmann, *Surf. Sci.* 395 (1998) 182.
- [9] D.M. Cox, P. Fayet, R. Brickmann, M.Y. Hahn, A. Kaldor, *Catal. Lett.* 4 (1990) 271.
- [10] R.J. Wolf, M.W. Lee, R.C. Davis, P.J. Ray, *Phys. Rev. Lett.* 73 (1994) 1971.
- [11] M.W. Lee, R.J. Wolf, J.R. Ray, *J. All. Comp.* 231 (1995) 343.
- [12] M.T. Reetz, M. Winter, R. Breinbauer, T. Thurn-Albrecht, W. Vogel, *Chem. Eur. J.* 7 (2001) 1084.
- [13] M. Suleiman, et al., in preparation.
- [14] M. Suleiman, N.M. Jisrawi, O. Dankert, M.T. Reetz, C. Bähz, R. Kirchheim, A. Pundt, *J. Alloys Comp.* 356357 (2003) 644.
- [15] L.D. Marks, *Rep. Prog. Phys.* 57 (1994) 603.
- [16] B.D. Hall, M. Flüeli, R. Monot, J.P. Borel, *Phys. Rev. B* 43 (1991) 3906.
- [17] S. Ino, *J. Phys. Soc. Jpn.* 21 (1966) 346.
- [18] A. Pundt, M. Dornheim, H. Guerdane, H. Teichler, H. Ehrenberg, M.T. Reetz, N.M. Jisrawi, *Eur. Phys. J. D* 19 (2002) 333.
- [19] M.N. Jisrawi, et al., in preparation.
- [20] T.B. Flanagan, B.S. Bowerman, G.E. Biehl, *Scripta Metall.* 14 (1980) 443.
- [21] B.J. Makenas, H.K. Birnbaum, *Acta Metall.* 28 (1980) 979.
- [22] R.B. Schwarz, A.G. Khachaturyan, *Phys. Rev. Lett.* 74 (1995) 2523.
- [23] J.W. Cahn, F. Larché, *Acta Metall.* 32 (1984) 1915.
- [24] A. Pundt, P. Pekarsky, *Scripta Mater.* 48 (2003) 419.
- [25] J.C.M. Li, A. Oriani, L.S. Darken, *Z. Phys. Chem.* 49 (1966) 271.
- [26] A. Pundt, *Habilitation Thesis*, Göttingen, 2001.
- [27] E. Salomons, R. Griessen, D.G. de Groot, A. Magerl, *Europhys. Lett.* 5 (1988) 449.
- [28] A. Züttel, Ch. Nützenagel, G. Schmid, Ch. Emmenegger, P. Sudan, L. Schlappbach, *Appl. Surf. Sci.* 162 (2000) 571.