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Journal of Alloys and Compounds 253–254 (1997) 175–180

Journal of ALLOYS AND COMPOUNDS

Deuterium Absorption in $Pd_{0.9}Y_{0.1}$ Alloy

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Abstract

Microgravimetric measurements are reported of the pressure–concentration dependence of deuterium in the palladium solid–solution alloy, $Pd_{0.9}Y_{0.1}$. An Intelligent Gravimetric Analyzer (IGA) was used and the measurements were made in the temperature range ($60\,°C \leq T \leq 100\,°C$). The results obtained revealed a hitherto unseen hysteresis effect in the absorption–desorption isotherm. This hysteresis is believed to be due to a reordering of the palladium–yttrium lattice driven by the hydrogen (deuterium) absorption. The second absorption/desorption cycle shows a wider hysteresis loop than the first but further cycles repeat the shape of the second loop. In-situ neutron diffraction measurements were also made on deuterated $Pd_{0.9}Y_{0.1}$ at 303 K. These data support the hypothesis that the hysteresis is due to an order–disorder transition involving the yttrium atoms in the metal lattice.

Keywords: Neutron diffraction; Phase diagram; Deuterium

1. Introduction

Palladium and its alloys are well known for their capability to absorb large quantities of hydrogen and its isotopes. Because of this, the use of such metals has been suggested in applications involving hydrogen purification and hydrogen isotope separation [1]. Palladium–yttrium alloys in particular have been shown to exhibit high permeation rates.

The first investigations of the solubility of yttrium and other rare-earths in palladium (Thomson [2] and Harris and Norman [3]), found that a solid–solution phase existed for the palladium–yttrium system up to a concentration of approximately 12.5 at.%.

The experiments reported in this paper are concerned with the hysteresis loop in the absorption–desorption isotherm for deuterium and how this relates to the structural changes as observed with neutron diffraction.

2. Experimental details

The palladium solid solution alloy, $Pd_{0.9}Y_{0.1}$ was prepared by melting the constituent metals in the appropriate proportions in an argon arc furnace. The starting materials were 99.999% Pd and 99.99% Y in ingot form. The ‘‘as-cast’’ buttons were annealed for periods in excess of fourteen days at a temperature of 950 °C and a vacuum of better than 10^{-6} mbar. The samples were then rolled to a thickness 0.1 mm. The samples were then loaded with hydrogen to relieve strain caused by the rolling process but despite this, frequent heat treatments were required to prevent ‘‘flowering’’. Prior to loading into the Intelligent Gravimetric Analyzer (IGA) system, the samples were mechanically abraded and a further vacuum annealing stage was performed. The IGA technique has been described elsewhere [4]. Hydrogen and deuterium isotherms were measured up to a pressure of 1 bar and in the temperature range $60\,°C \leq T \leq 100\,°C$. Before each run the sample was annealed at 700 °C and cooled slowly to the appropriate temperature.

Neutron diffraction measurements were also performed on this sample at the D1B neutron diffractometer at the ILL, Grenoble. The sample was deuterated in-situ, so that the diffraction pattern could be recorded at progressively higher concentrations. The sample temperature was 60 °C. The sample can used was made of aluminum, which later proved to be somewhat inconvenient, because, at the highest deuterium concentrations, the sample lattice parameter is nearly equal to that of the aluminum, and both are FCC structures. The instrument was set up for 2-theta

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PII S0925-8388(96)03078-2

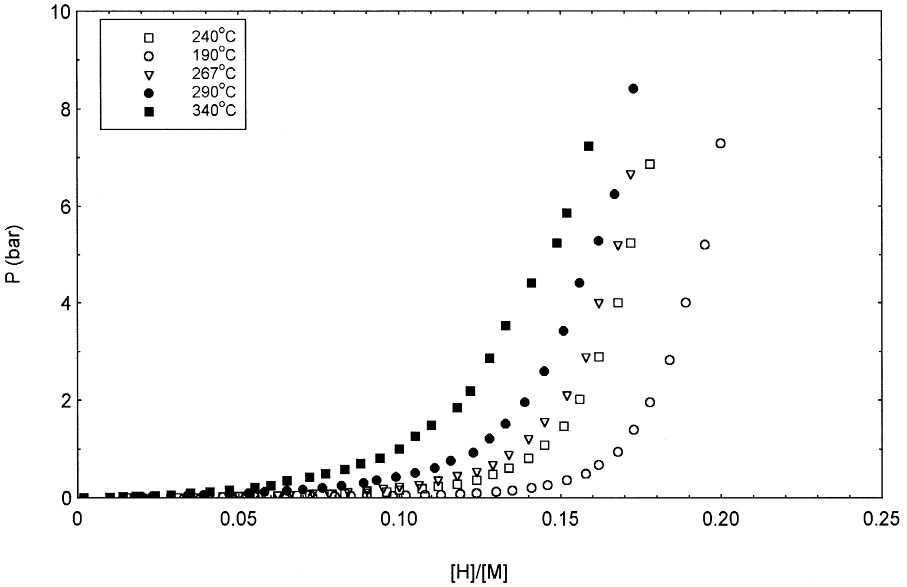

Fig. 1. The isotherms describe the absorption of hydrogen measured at different high temperatures in $Pd_{0.9}Y_{0.1}$.

scans in the range 39.2 degrees to 119.0 degrees, in 0.2 degree steps, giving 400 channels.

3. Results and discussion

Fig. 1 shows a set of absorption isotherms measured at higher temperatures (190 °C≤T≤340 °C). In the low partial pressure region, a high stability solid solution is observed. This is best illustrated by the Sievert's plot, Fig. 2, which shows the marked temperature dependence of the solubility measurements and demonstrates that Sievert's law is only obeyed as the concentration tends to zero. For higher concentrations, a positive deviation from ideal behaviour becomes increasingly more marked as the temperature is lowered. In the low temperature range, Fig. 3, 60 °C≤T≤100 °C, all the isotherms exhibit hysteresis during absorption/desorption of hydrogen (deuterium). Several hysteresis loops were measured at each temperature. It is noticeable that, in all cases, the first absorption isotherm, just after the anneal, follows a different path to subsequent absorptions, whereas all the desorption isotherms follow very similar paths. This suggests that the first absorption modifies the lattice structure until the

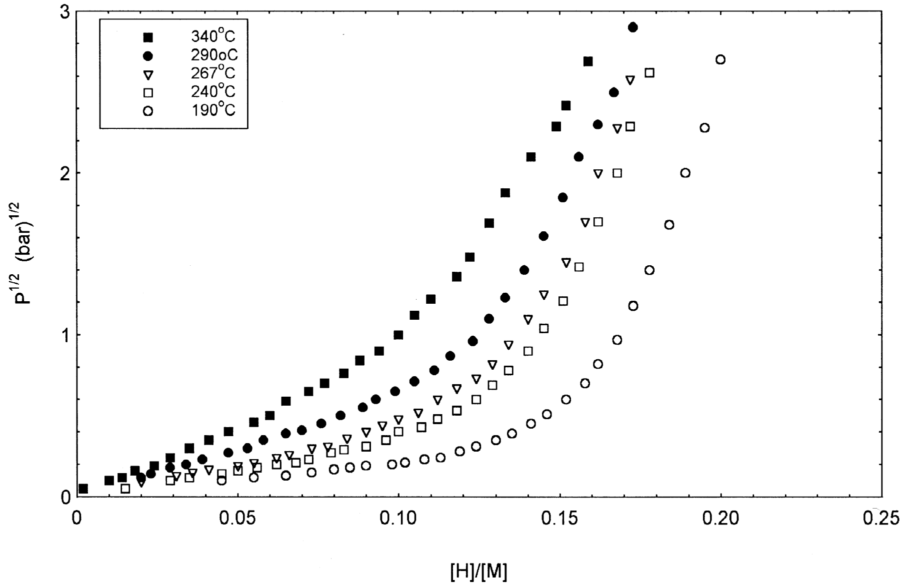

Fig. 2. Sievert's plots of the isotherms for the absorption of hydrogen in $Pd_{0.9}Y_{0.1}$.

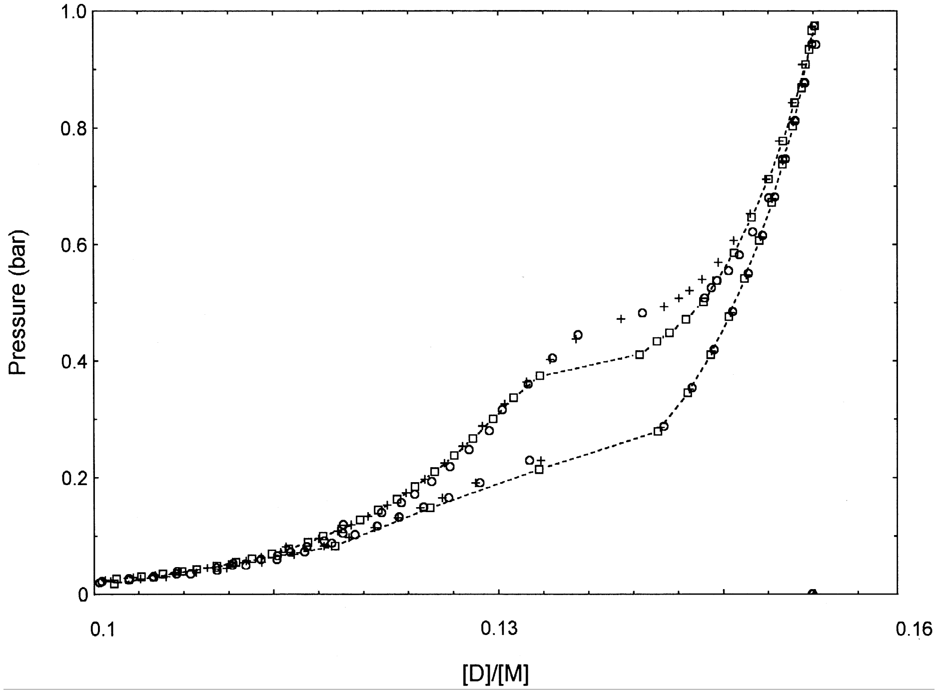

Fig. 3. The isotherms measured at 60 °C in $Pd_{0.9}Y_{0.1}$ showing the hysteresis shapes after several cycles.

sample is reannealed. The hysteresis loops appear at slightly higher concentrations with hydrogen than with deuterium. One should also notice that the concentration of hydrogen for which hysteresis occurs is almost independent of temperature. Because H is more soluble than D, the concentration required for hysteresis is attainable within the 0–1 bar pressure range of the experiment up to higher temperatures with hydrogen. (The equilibrium concentration at 1 bar decreases as the temperature increases for each gas isotope so that there is a temperature at which the required concentration can no longer be reached). No hysteresis was observed at 100 °C or above with deuterium, and the effect was smaller than for hydrogen at 90 °C, whereas the effect was still strong at 110 °C with hydrogen.

It is thought that this hysteresis behaviour is caused by an order–disorder transition involving the yttrium atoms in the metal lattice, which is driven by the Y–Y repulsion caused by the size mismatch. Stonadge [5] points out that ordering of yttrium atoms has been observed in this alloy, and says that the ordered sample can be cycled reversibly several times, providing the critical temperature (at which the sample disorders) is not exceeded. However, that work was carried out at higher temperatures than the present study, and so the present hysteresis was not previously observed. At low temperatures, higher gas concentrations are possible, and it may be that these higher concentrations are sufficient to produce reversible order–disorder transitions.

In-situ neutron diffraction measurements were also performed on the deuterated $Pd_{0.9}Y_{0.1}$ sample on the D1B instrument at the ILL. Fig. 4 shows the diffraction pattern obtained, where each pattern corresponds to a different concentration of absorbed deuterium. The patterns nearest to the top have the highest [D]/[M] ratios. The difference in background is due to the incoherent scattering from the deuterium atoms which, as expected, increases with deuterium concentration. The two largest peaks, which go off the top of the graph are the (200) and (111) peaks of the FCC $Pd_{0.9}Y_{0.1}$ lattice. The broad feature around $d\sim 2.85$ Å is diffuse scattering, presumably arising from the distance between deuterium atoms. The diffuse nature of this scattering indicates that the deuterium structure is not perfectly ordered, but exhibits short range order (SRO). Fig. 5 shows the detail of the diffuse scattering at $d\sim 2.85$Å. The narrow peak in the center is believed to be a superlattice reflection caused by ordering of the sample beyond a single unit cell. This peak indexes to (110) relative to the FCC host lattice, a reflection that is forbidden for pure FCC lattices. We believe that the presence of yttrium in the sample causes ordering into a superlattice having a unit cell of dimensions $2a$ in each direction, where ''a'' is the lattice parameter of the metal ($a=3.98$ Å). the reflection in question is then the (220) reflection of the superlattice, which is now allowed. The composition of the superlattice, if perfectly formed, would be Pd_7Y a derivative of the Cu_3Au type structure. In the latter structure, the substituted yttrium atoms form an FCC lattice twice as large as the metal lattice. The important point to note is that the superlattice reflection persists at all deuterium contents. Thus the hysteresis is not due to an order–disorder transition so we must presume that it is due

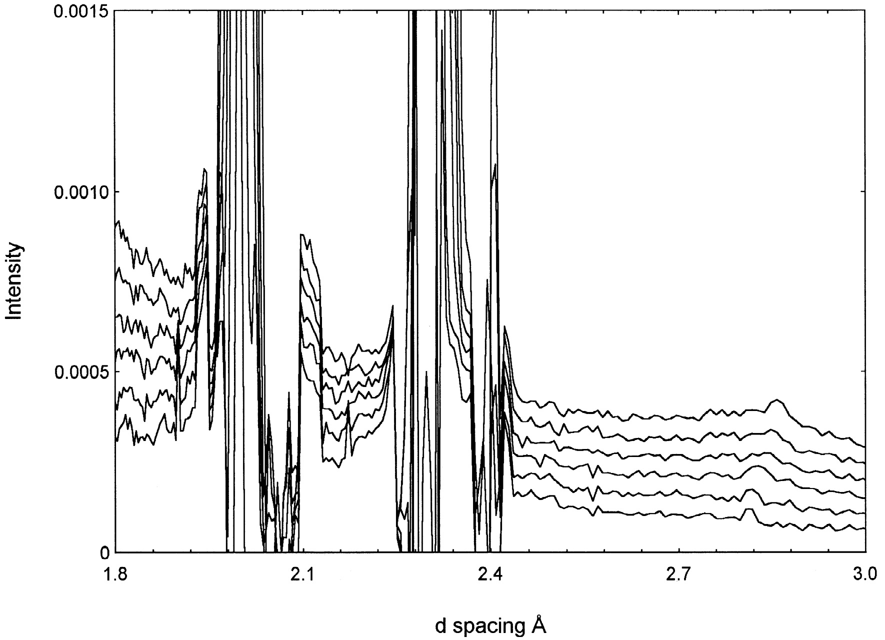

Fig. 4. Magnified view of the $Pd_{0.9}Y_{0.1}$–D diffraction patterns measured in-situ at 60 °C for different deuterium concentrations.

to a change in short range order possibly of the palladium on the yttrium sublattice.

Fig. 6(a) and Fig. 6(b) show, respectively, the evolution of the (200) and (111) peak as the deuterium concentration increases. Note that as [D]/[M] increases, not only does the peak move to the right due to the expansion of the lattice, but it first becomes lower and broader before renarrowing and ending up with greater intensity for the (200) and lower for the (111) peak. These changes of the intensities ratio between the (200) and (111) peaks are as would be expected to result from the introduction of deuterium to the octahedral sites. They also seem to happen at around the same deuterium concentration where the hysteresis start occurring. These changes are believed to be a confirmation of the order–disorder transition involving the yttrium atoms in the metal suggested by

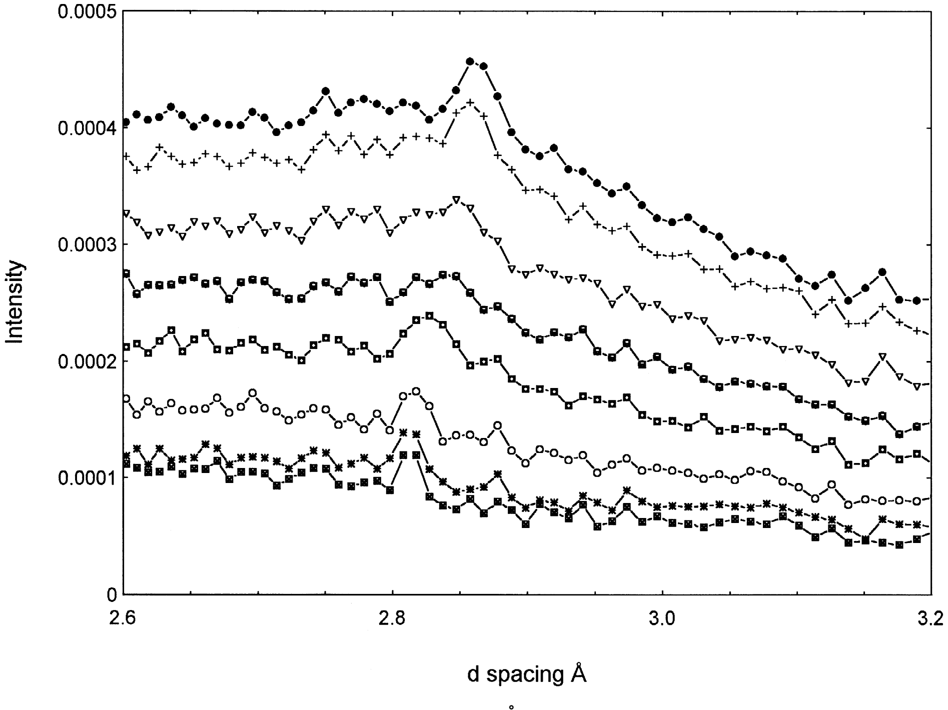

Fig. 5. This picture shows the detail of the diffuse scattering around $d=2.85$ Å. The narrow peak in the centre represents the superlattice reflection.

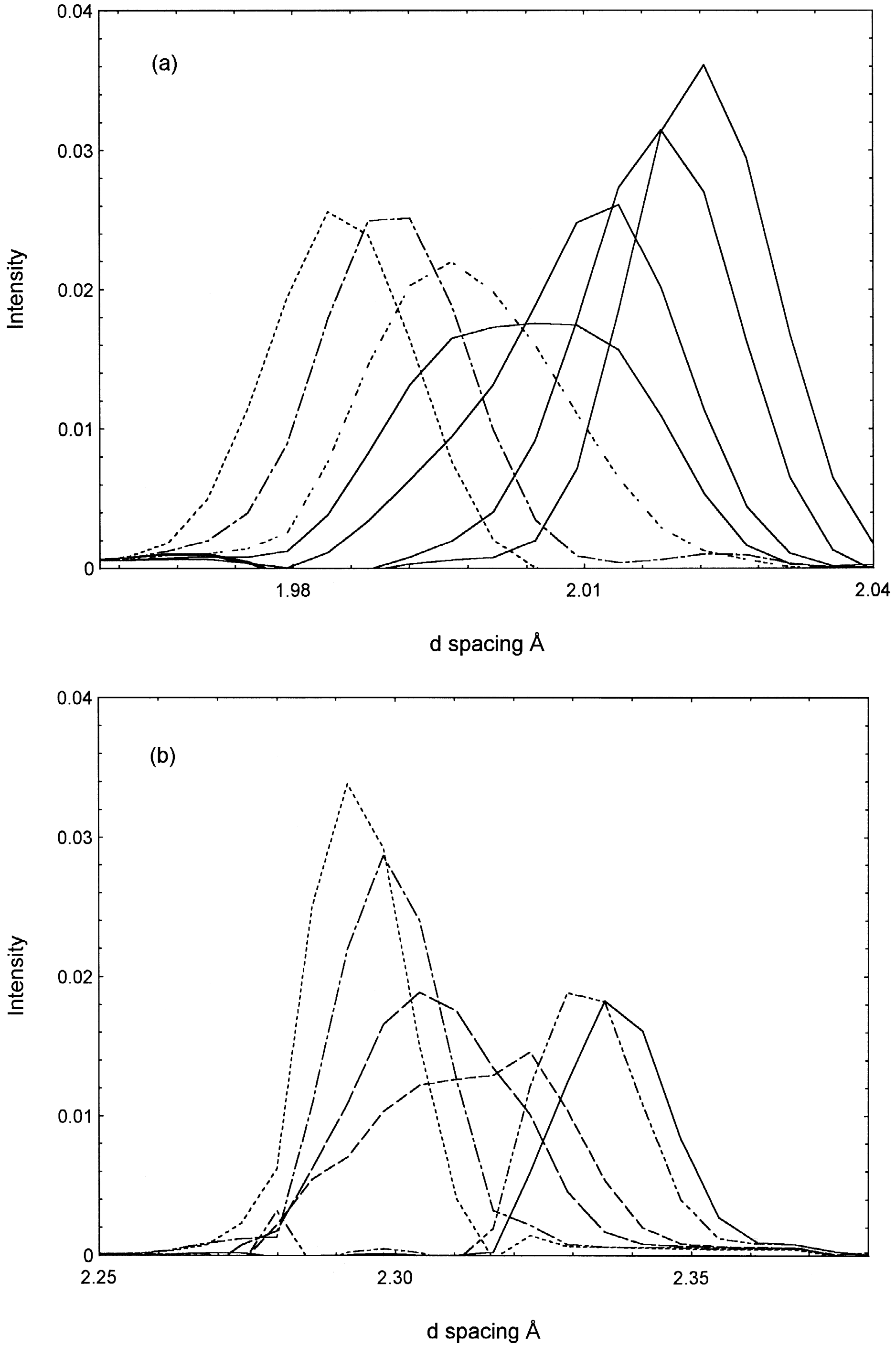

Fig. 6. The figures (a) and (b) show, respectively, the evolution of the (200) peak and (111) peak as the deuterium concentration is increased.

Stonadge [4]. The increase in the lattice parameter is shown as a function of hydrogen content in Fig. 7.

4. Conclusion

The hysteresis loop we have observed in the $Pd_{0.9}Y_{0.1}$-H system is quite different from that observed in Pd–H, in that the plateau loops have sloping tops and bottoms, not the flat sections seen in β Pd–D(H). In the palladium hydride system, the plateaus are attributed to the α–β phase separation. In that case the two phases are characterized by two distinct lattice constants and hydrogen concentrations and the transition is known to be driven by long-range stresses. In contrast, in the present case, diffraction data (Fig. 7) show us that there is no phase separation. We would therefore attribute the loop in the present system to a structural transition.

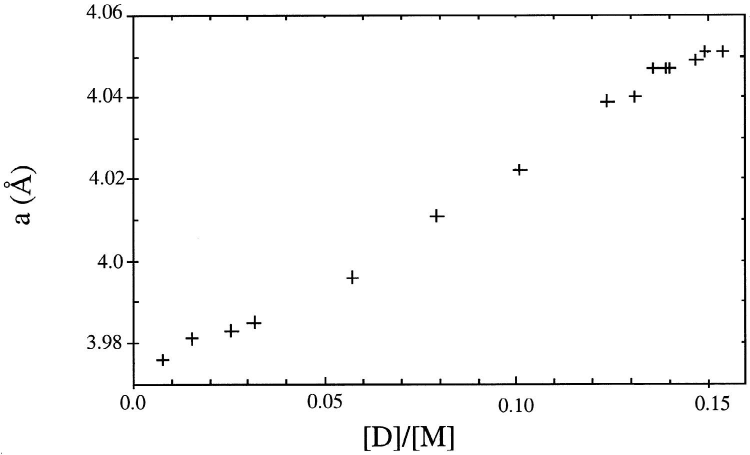

Fig. 7. This shows the linear increase of the lattice parameter as function of the deuterium concentration.

We can further conclude from the fact that the superlattice reflection persists across the absorption isotherm that the transition is not an order–disorder process in the $Pd_{0.9}Y_{0.1}$ lattice. It would therefore seem likely that we are seeing changes in the short range order of palladium atoms on the yttrium sublattice (because our alloy has 10% Y and the superlattice would be stoichiometric at 12.5% Y). Thus, in the pure metal lattice, there will be repulsive interactions between Pd atoms on the Y sublattice (because of the atom size mismatch) which are much weaker in the hydrogenated phase because the hydrogen atoms will cluster around these Pd, hence compensating for the local stress. Thus the palladium on the yttrium sublattice will be much more disordered in the hydrogenated lattice.

Acknowledgments

The authors are grateful to Professor I.R. Harris for valuable discussions during the writing of this manuscript.

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