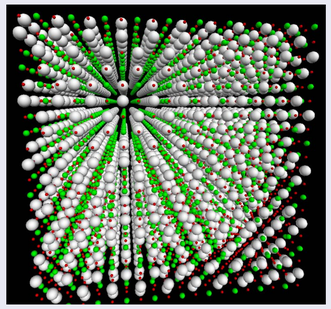
University of Salford MANCHESTER

Monte-Carlo Simulations of Hydrogen Isotopes in Palladium

Ian Robinson : supervisor Professor Keith Ross

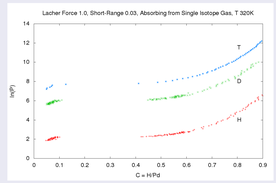
Overview

Extensive Monte-Carlo investigations on the Palladium Hydride system have been performed. It is demonstrated that a simple long-range concentration dependent attractive force reproduces the form of the pressure composition isotherms well. Short range pairwise repulsive forces reproduce much of the hydrogen ordering seen within the lattice. A suitable scaling between the long and short range forces has been found which appears to reproduce both the isotherms and short-range ordering to a reasonable degree. Programs have been written to generate virtual diffractograms in 1 d and 2d in order to observe ordering in the simulations. Studies have been performed of the isotope dependence of adsorption rate and separation factor by accounting for the differing zero point energies of the three hydrogen isotopes .



Lacher Model

John Lacher (1937) proposed that the two phase region resulted from a long-range attraction between protons. As hydrogen is added the increasing lattice distortion leads to an attractive force via some unknown mechanism. This correctly reproduces the form of the pressure composition curves however does not reproduce short-range ordering which is likely due to to short range repulsion between the protons. It has been shown that a model combining the simple Lacher concentration dependent attraction with pairwise short-range repulsion can reproduce both pressure composition curves and short-range ordering.

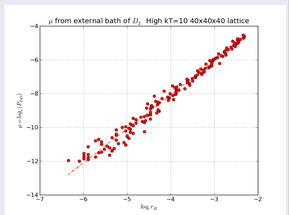


GCMC Simulation: Variation of Plateau Pressure with H,D,T at 320K.

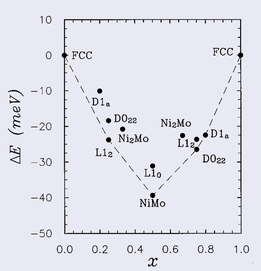
Sievert's Law

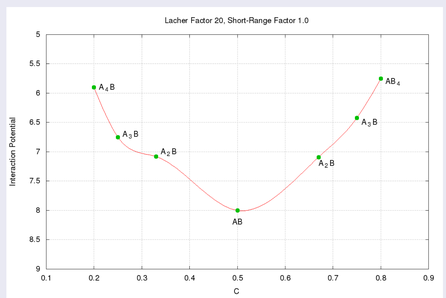
Clearly the PdH system does not conform to Sievert's Law across the composition range. At low concentrations in the α phase, however, it does (Caravella:2010).Simulations here generated $C \propto P^{0.498\mu}$.

This held for long-range 'Lacher' forces only, short-range repulsion only and a combination of the two. This was to be expected as at low concentrations or high temperatures, the long and short-range forces may be neglected and the system approaches ideality.



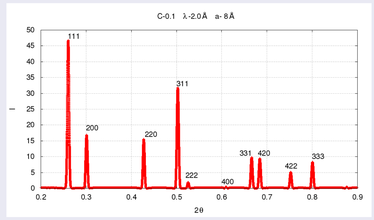
Formation Energies





Formation energies for various Pd_AH_B structures - CMC simulations employing both long and short-range forces *(right)*. The similar fit to total energy studies *(left)* may imply that these models are valid.

Simulated Diffraction Patterns



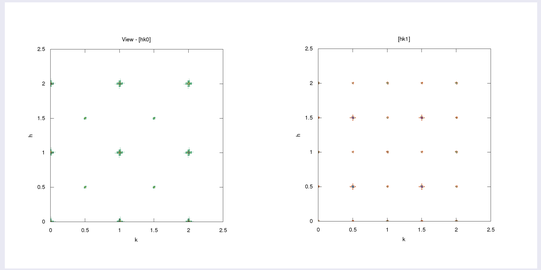
Virtual Debye Diffraction Pattern of H in Pd, hkl all odd or all even as expected for FCC structure

Two approaches were employed to simulate diffraction patterns from lattices produced by the simulations. The first employed the Debye scattering equation for powder samples. This is computationally very efficient at producing a 1d pattern though directional information is lost

$$I(q) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} f_i f_j \frac{sin(2\pi q r_{ij})}{2\pi q r_{ij}}$$

where f_i, f_j are the scattering factors of the respective atoms and q, r_{ij} are equal to $|\vec{q}|$ and $|\vec{r_{ij}}|$ respectively.

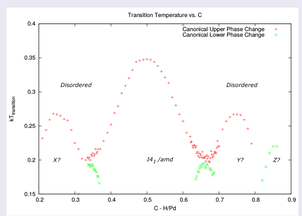
The technique used here for the contour 2d plots involves summing $e^{i\left(\vec{G}\cdot\vec{r_i}\right)}$ over a range of G_x and G_y.

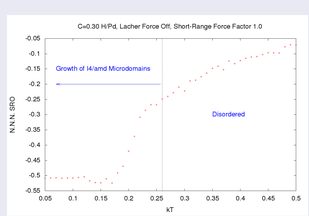


C=0.76 , possible superlattice reflections at (0.5,0.5,0) – same at 0.78

This permitted the investigation of subtle short-range ordering by comparing simulated diffraction patterns from simulations with both ideal ones and those from experiment.

Phase Diagram

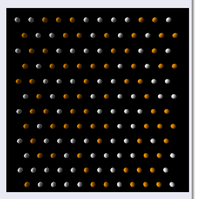




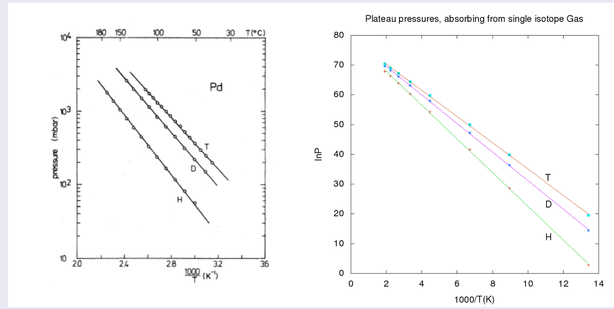
At concentrations below $c \simeq 0.5$ the long-range Lacher attraction appears to have little effect upon the structures observed i.e. the short-range forces dominate. As above $c \simeq 0.7$ the Lacher attraction would appear to add more complex structures than the short-range forces alone. Simulations over a wide ratio of forces did not reproduce the Ni_4Mo structure, however there were faint hints from visual inspection that it may have started to form. Interestingly, C.M.C. runs in which the temperature of lattices populated with Ni_4Mo was raised indicate that the temperatures at which this structure disappeared were unaffected by the strength of the Lacher attractive force. This may imply that more localised short-range forces need to be invoked to explain the formation of this phase. Possibly a combination of localised attractive as well as repulsive effects or triplet rather than simple pairwise interactions.

Zero Point Energy

Palladium Hydride displays an unusual *reverse isotope effect*. Simplistically one would assume that Deuterium and Tritium's higher masses and thus lower vibrational frequencies would lead to lower diffusion rates and lower superconducting temperatures than for protium. In reality the inverse is seen. The diffusivity effect is assumed to be due to marked differences in their respective zero point energies in both the gas and solid phases. Modeling permitted different ZPEs in the gas and solid phases. Fig shows clustering of isotopes due to differing ZPE. [420] plane $I4_1/amd$, *protium orange, deuterium white*



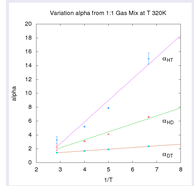
Variation of Plateau Pressure with Isotope



Left- Experimental results Lasser (1982) : *Right*- GCMC Simulation for H,D and T

The model would appear to reproduce experimental results of the variation in plateau pressure in the $\alpha - \beta$ region tolerably well..

Variation of Separation Factor with Temperature



Separation factors were measured with a GCMC simulation where the pressure was lowered such that the lattice concentration dropped from a 100% fill of the two isotopes in a 1:1 ratio. The external gas was also at a 1:1 composition. α varied approximately linearly over a temperature range of $\sim$ 100K to 400K though diverged outside this range. This may be compared to the results of Andreev where the figures are obtained over a similarly narrow range.

Summary

A simple model of the Pd-H system employing a combination of long-range concentration dependent attractive forces and pairwise repulsive forces out to the fourth nearest neighbour has been comprehensively investigated. These has been extensively tested with over 2000 runs at relatively high resolution and lattice size - typically $10^4 \rightarrow 10^5$ atoms. Programs have also been developed to produce virtual diffraction patterns in 1 and 2d as well as interactive programs to examine the lattice structure in pseudo 3d.
It has been found that a combination of attractive force rather stronger than the repulsive force reproduces the pressure composition isotherms whilst still permitting short-range ordering to occur. Most of the expected phase structures appeared however there was no conclusive sign of the Ni_4Mo. However simulated diffraction studies showed signs of an unusual structure faintly forming at $C \sim 0.8H/Pd$. The model did not generate signs of hysteresis in the pressure decomposition curves implying that a more complex model needs to be considered.
Incorporating differing zero point energies for the three isotopes in both the gas and solid phases produced variation in separation factor in-line with experiment. The simulations however produced tracer diffusion coefficients for pure D systems higher than expected.