The optic mode frequencies and solubilities of hydrogen in ordered and disordered Pd$_3$Mn

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Abstract. The solubility of hydrogen in the vacuum-annealed form of Pd$_3$Mn, i.e., the long-period superstructure form, is much greater than that in the disordered form of the same alloy as determined from solubility measurements below the order–disorder temperature. For example, at 400 K the solubility in the ordered form is ≃18 times greater than that in the disordered form at the same, small hydrogen pressure. This difference in solubilities is principally due to the greater exothermicity of hydrogen solution in the ordered form.

The optic model frequencies of protium and deuterium have been measured by inelastic neutron scattering and the frequencies for both forms of the alloy are found to be somewhat greater than for pure palladium–hydrogen (α-phase) and they are consistent with the occupation of octahedral interstices. The observed second harmonics and isotope shifts show that the local potential for hydrogen bound in both the ordered and disordered forms is highly anharmonic, resembling that of the unusual potential found for hydrogen in pure palladium.

1. Introduction

It has been found by Phutela and Kleppa (PK) [1] that the hydrogen solubility behaviour differs in the ordered (LPS (long-period-superstructure) type of order [2]) and disordered forms of Pd$_3$Mn. PK determined thermodynamic data from pressure–composition–temperature data and from calorimetric measurements above and below the order–disorder temperature; however, no direct comparisons of the hydrogen solubilities in the two forms of the alloy were made because measurements for the disordered form were made above T_c and for the ordered form they were made below. From extrapolation of the data from above and from below the critical temperature of ≃800 K PK concluded that there was a greater solubility in the ordered form. Recently the solubilities in both forms have been measured below the critical temperature [3] and these results have confirmed the predictions of PK which were based on their measurements above and below the critical temperature.

In the present research thermodynamic data are derived from hydrogen solubility results for both forms of Pd$_3$Mn below the critical temperature, T_c, where the solubilities can be directly compared and where the differences in solubilities are greater than found near T_c [1]. These solubility results will be considered in the light of the vibrational frequencies of hydrogen measured by inelastic neutron scattering.

It should be noted that this alloy system is a very useful one for fundamental studies of hydrogen solubilities because they are sufficiently large at pressures $\leqslant 1$ atm to allow the determination of detailed thermodynamic data from pressure–composition–temperature measurements. For the Pd_3Fe–H system Flanagan and co-workers [4] also found a greater solubility in the ordered form, but for this system the solubilities were very small at pressures of hydrogen $\leqslant 1$ atm, and detailed thermodynamic data could not be obtained. The ordered Pd_3Fe alloy has the $L1_2$ structure with 0.25 of the octahedral interstices surrounded only by Pd nearest neighbours, and in the disordered form, assumed to be completely random, there are 0.178 such interstices. By contrast, for ordered Pd_3Mn, which has a long superstructure, there are 0.125 octahedral interstices. (This was assumed to be 0.25 by PK [1] and therefore their discussion of the configurational entropy for hydrogen solution is in error. Recently it was discovered that the $L1_2$ ordered form of this alloy, with 0.25 Pd-rich interstices, can also be prepared, but only in the presence of relatively high hydrogen pressures [5]).

As an aid to understanding the differences in hydrogen solubility between the ordered and disordered forms and also to obtain information on the nature of the potential of the hydrogen bond in interstices in the ordered and disordered lattices, we have measured optic mode frequencies of the dissolved protium and deuterium by using inelastic neutron scattering.

2. Experimental details

Solubility data were determined from pressure changes in a conventional Sieverts-type apparatus. The disordered alloy used for solubility measurements was prepared by rapid quenching from $\simeq 1100$ K into ice–water while simultaneously the quartz containing vessel was broken; the disordered alloy employed for neutron scattering was prepared by cold-working an Pd_3Mn alloy; solubility measurements showed this to be an effective way to introduce disorder. The ordered samples were prepared by cooling slowly from 1273 K *in vacuo* for a two-week period.

The neutron vibrational spectra for ordered and disordered Pd_3MnH_x (D_x) were measured using the BT-4 crystal spectrometer at the National Bureau of Standards Reactor, which is equipped with a high-intensity, low-background beryllium filter analyser. These measurements provide direct information on the density of vibrational states for the hydrogen optic modes.

3. Results and discussion

3.1. Inelastic neutron scattering data

Figure 1 shows the inelastic scattering spectrum for the disordered alloy $Pd_3MnH_{0.03}$ at 295 K; at this hydrogen content it can be shown from solubility measurements that only the dilute protium phase is present. The optic mode peak due to protium is centred at 74 meV. It is clear that, as would be expected, protium occupies the octahedral interstices because if it were in tetrahedral interstices, the frequency would be much greater [6]. By comparison, the protium optic mode frequency for the dilute α-phase in palladium is centred at 69 meV [7]. The band that is seen in figure 1 at higher energies is primarily due to the 'overtone' of the 74 meV peak, and it is centred at $\simeq 161$ meV and thus
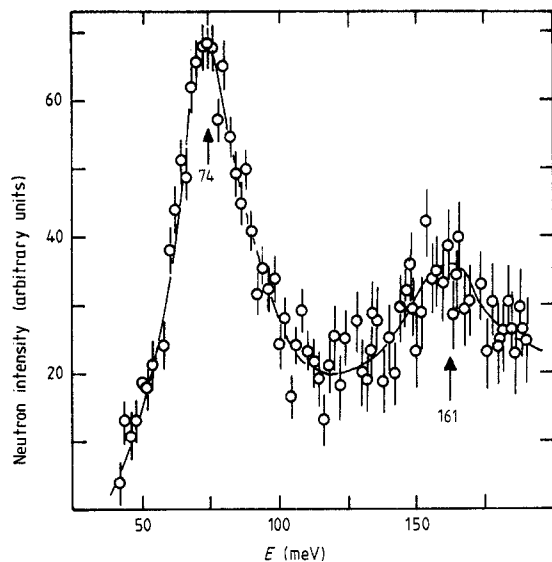
Figure 1. The neutron inelastic scattering spectrum for the disordered alloy $Pd_3MnH_{0.03}$ measured at 295 K.
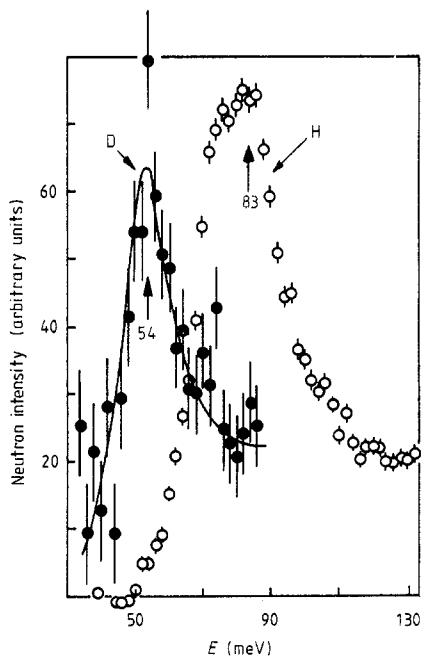

Figure 2. Neutron inelastic scattering spectra for the ordered alloys (LPS-type order) $Pd_3MnH_{0.4}$ and $Pd_3MnD_{0.4}$ measured at 295 K.

provides a value greater than 2 ($\simeq 2.2$) for the ratio $\hbar\omega(0 \to 2)/\hbar\omega(0 \to 1)$ and this indicates a distinctly anharmonic potential.

The inelastic neutron spectra taken at 295 K for the alloys $Pd_3MnD_{0.4}$ and $Pd_3MnH_{0.4}$, where the metal sublattice is ordered, are shown in figure 2, and the former alloy exhibits a DOS peak centred at 54 meV. The DOS for $Pd_3MnH_{0.4}$ shows evidence of splitting into two peaks centred at 76 and 83 meV. The higher-frequency peak is taken as corresponding to protium in the α-phase and the lower-frequency peak may arise from protium in a β-phase. Judging from detailed hydrogen isotherm measurements, it is quite likely that $Pd_3MnH_{0.4}$ forms a protide phase at this temperature and content and, again judging from the isotherms, the system may be just below the critical point for second-phase formation, and therefore the protium content of any protide phase that is formed would not differ much from that of the coexisting dilute phase. Because of the isotope effect on the critical temperatures in pure palladium, it would be expected that the situation would be similar here and the $Pd_3MnD_{0.4}$ alloy would not form a deuteride phase at this temperature where the H alloy just forms a protide phase. The observed peaks are broad ($\simeq 15$ meV for D and H where, for the latter, the width has been estimated as half of the total width of the two overlapping peaks).

Of interest is the unusual isotope shift $\hbar\omega(H)/\hbar\omega(D) = 1.54 \pm 0.03$ observed for the average frequencies. This shift provides further direct evidence for a very anharmonic potential and it can be noted that the potential observed for H in the α-phase of pure palladium [7] is also quite anharmonic. The isotope shift for α-phase pure palladium is 1.49 $\pm$ 0.02 [7], so the values are just within experimental error of each other. The fundamental frequencies of the alloy are quite different from that of hydrogen in
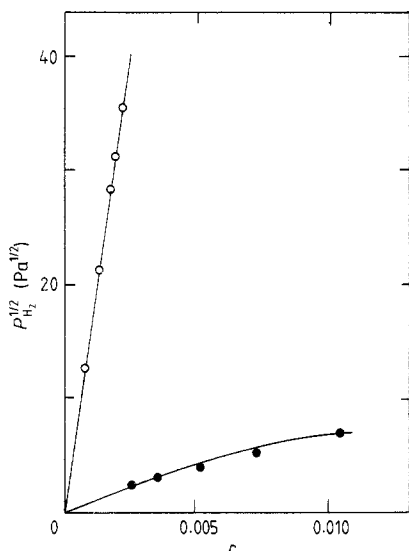
Figure 3. Hydrogen solubility measurements for ordered (LPS-type) and disordered Pd$_3$Mn at 457 K: ●, ordered alloy; ○, disordered alloy.

palladium, i.e., $\hbar\omega = 69$ and 46.5 meV for α-PdH$_x$ and α-PdD$_x$, respectively. The anomalous ratio discussed above of the fundamental and overtone peak energies for H in the disordered alloy is also consistent with a potential analogous to that in pure palladium. It has been recently found from neutron diffraction that D occupies mainly the octahedral interstices in ordered Pd$_3$MnD$_{0.6}$ with only palladium atoms as nearest neighbours [8] which is quite consistent with the above results if the frequency is determined principally by the nearest-neighbour environment.

As pointed out by Oates and Flanagan [9] optic mode frequencies measured by neutron scattering for protium in palladium tend to be smaller than those deduced indirectly from thermodynamic measurements of the isotopic ratios of protium and deuterium using the assumption that the ratio of the Einstein temperatures of H and D is $\sqrt{2}$ where the isotope ratio is given by $RT\ln(p_{H_2}/p_{D_2})^{1/2}$ and this is evaluated at a constant hydrogen content. PK [1] used measured isotope ratios for the Pd$_3$Mn alloys to deduce fundamental vibrational frequencies of 80.6 meV for the ordered alloy and 106.6 meV for the disordered one at 700 K. These values are, however, reversed from the true order where the ordered alloy has a larger frequency than the disordered one (figures 1 and 2). The use of the observed isotope shift of 1.54, instead of $\sqrt{2}$, gives better agreement with the observed isotope ratios for the Pd$_3$Mn alloys using aharmonic oscillator approximation; earlier this same approximate value was also found to give good agreement for isotope ratios for pure palladium in this temperature range [9].

3.2. Hydrogen solubilities

A typical difference in hydrogen solubility between the ordered (LPS-type) and disordered forms of the Pd$_3$Mn alloy is illustrated by two isotherms at 458 K in figure 3 where it can be seen that there is a much greater solubility in the ordered form. Such solubility data were employed to determine values of ΔH_H^0 and ΔS_H^0, which are the standard relative partial enthalpy and entropy of solution of hydrogen, respectively, at conditions of infinite dilution of hydrogen in the alloy; relative refers to the hydrogen gas at 1 atm pressure [10]. In order to determine ΔS_H^0 the value of β must be known

Table 1. Thermodynamic parameters for hydrogen solution in ordered (LPS-type) and disordered Pd₃Mn at 450 K.

Thermodynamic values	Pd [11]	Pd₃Mn (LPS order)	Pd₃Mn (disordered)
ΔH_H^0 (kJ/mol H)	-8.6	-33.2	-22.8
ΔS_H^0 (J K^{-1}/mol H)	-52.0	-61.2 (-75.7)	-60.5 (-77.8)
S_H^0 (J K^{-1}/mol H)	19.2	10.0	10.7
S_H^{vib} (J K^{-1}/mol H)	13.6	11.6	10.2
($S_H^0 - S_H^{vib}$) (J K^{-1}/mol H)	5.6	-1.6	0.5

where β is the number of interstices available for hydrogen occupancy per metal atom at the pressures employed (equation (1))

$$-\partial RT \ln[p_{H_2}^{1/2}(\beta - r)/r]/\partial T = \Delta S_H^0 = S_H^0 - \tfrac{1}{2}S_{H_2}^0 \tag{1}$$

where $r =$ H/metal. For pure palladium $\beta = 1$, but for palladium-rich alloys its value was not known until Andersson and co-workers [8] recently found that the hydrogen enters the interstices surrounded only by palladium nearest neighbours in the ordered form of Pd₃Mn. Table 1 shows the results for an average temperature of 450 K together with values for the α-phase of pure palladium [11].

Table 1 shows that the solution of protium is much more exothermic in the ordered form than in the disordered form and this accounts for the former's greater solubility. The values of ΔS_H^0 shown in parentheses have been calculated using $\beta = 1$ and those not in parentheses have been calculated using 0.125 and 0.178 for the ordered and disordered alloys, respectively. It can be seen that the use of the β-values based on the fraction of available interstices surrounded by palladium nearest neighbours yields entropy values for both alloys closer to the value for pure palladium and supports the idea of the selective occupation of interstices in palladium alloys.

The higher optic mode frequencies found for the Pd₃Mn alloys as compared to palladium means that the values of ΔS_H^0 should be smaller in these alloys than in palladium and this is what is observed (table 1). It seems that the values of S_H^0 for the alloys can be accounted for quite well by a vibrational entropy calculated from the Einstein model at 450 K (S_H^{vib}; see table 1) whereas the value of S_H^0 for pure palladium cannot.

It has been recently observed that the interstices with only palladium atoms as nearest neighbours are the favoured ones in the ordered Pd₃Mn alloy [8]. This is consistent with the observed values of the entropies for solution of hydrogen found here. It is clear from the results shown in table 1 that the enthalpies of solution of hydrogen must depend upon factors other than the nearest-neighbour environment of the interstices even though the local potential experienced by hydrogen in Pd₃Mn alloys appears to be similar in shape to that in pure palladium metal. This is also believed to be the case for the Pd₃Fe alloy where it has been shown that the electronic heat capacities are in the opposite direction from what would be expected on the basis of the observed increased solubility in the ordered alloy [12]. It is believed that local effects predominate in the increased solubility of the ordered alloys but these local effects involve more than the first-nearest neighbours.

Acknowledgments

References

[1] Phutela R C and Kleppa O J 1981 *J. Chem. Phys.* **75** 4095
[2] Watanabe D 1962 *Trans. Japan. Inst. Met.* **3** 234
[3] Baba K, Sakamoto Y, Flanagan T B, Kuji T and Craft A P 1987 *Scr. Metall.* **21** 299
[4] Flanagan T B, Majchrzak S and Baranowski B 1972 *Phil. Mag.* **25** 257
[5] Baba K, Niki Y, Sakamoto Y, Flanagan T B and Craft A P 1987 *Scr. Metall.* **21** 1147
[6] Khoda-Bakhsh R and Ross D K 1984 *J. Phys. F: Met. Phys.* **12** 15
[7] Rush J J, Rowe J M and Richter D 1984 *Z. Phys.* B **55** 283
[8] Ahlén P-J, Andersson Y, Flanagan T B and Sakmoto Y 1989 *Z. Phys. Chem., NF* at press
[9] Oates W A and Flanagan T B 1977 *J. Chem. Soc. Faraday Trans.* I **73** 407
[10] Oates W A and Flanagan T B 1981 *Prog. Solid State Chem.* **13** 193
[11] Clewley J D, Curran T, Flanagan T B and Oates W A 1973 *J. Chem. Soc. Faraday Trans.* I **69** 449
[12] Bechman C A, Wallace W E and Craig R S 1973 *Phil. Mag.* **27** 1249