Pressure dependence of T_c for Pd$_{0.93}$Ag$_{0.07}$H$_c$(D$_c$) up to 8 GPa, synthesised and measured in a diamond anvil cell

Pressure dependence of T_c for $Pd_{0.93}Ag_{0.07}H_c(D_c)$ up to 8 GPa, synthesised and measured in a diamond anvil cell

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Abstract. We have synthesised hydrides of $Pd_{0.93}Ag_{0.07}$ at hydrogen pressures up to 8 GPa in a diamond anvil cell and measured *in situ* the pressure dependence of the superconducting transition temperature T_c. We find that $T_c = 11.4$ K and $\partial(\ln T_c)/\partial(\ln V) = 10.2$ for $Pd_{0.93}Ag_{0.07}D_c$ and that $T_c = 8.8$ K and $\partial(\ln T_c)/\partial (\ln V) = 11.5$ for $Pd_{0.93}Ag_{0.07}H_c$, both loaded at 8 GPa. The measured T_c-values and their pressure dependences are similar to those for Pd–H(D) and are well described by a theory based on the Allen–Dynes formalism. The influence of disorder on T_c is discussed and a lattice-gas model is used to estimate the contents after loading. Most available experimental data as well as theoretical considerations support the idea that higher T_c-values than found previously in the Pd–Ag–H system could be possible if disorder due to hydrogen or deuterium implantation can be suppressed.

1. Introduction

Shortly after the discovery of superconductivity in the Pd–H system by Skoskiewicz (1972), an inverse isotope effect was discovered at the superconducting transition temperature T_c by Stritzker and Buckel (1972). The theoretical explanation involved a subtle combination of several ingredients and is still a matter of interest (Ganguly 1973, Miller and Satterthwaite 1975, Papaconstantopoulos and Klein 1975, Papaconstantopoulos *et al* 1978, Karakazov and Maksimov 1978, Griessen and de Groot 1982, Laufer and Papaconstantopoulos 1985, Zhernov and Drekhsler 1985, Hemmes *et al* 1989a).

Experiments by Buckel and Stritzker (1973) and Stritzker (1974) showed that much higher transition temperatures (up to about 17 K) could be obtained by high-energy implantation of hydrogen in alloys of palladium with a noble metal. The theoretical work of Papaconstantopoulos *et al* (1979) and Laufer and Papaconstantopoulos (1985, 1986) suggested, however, that even higher T_c-values should be possible in the Pd–noble metal–H system. A possible cause for the discrepancy could be the implantation technique used by Stritzker to prepare the hydrides. This technique gives an inhomogeneous distribution of the hydrogen in the sample and the high-energy protons damage the lattice. On the contrary, it was found that the T_c values for palladium hydrides

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prepared with the implantation technique are the same as with other preparation techniques. Furthermore it was found that palladium can become superconducting after irradiation with α-particles (Stritzker 1978, 1979).

One way to avoid possible side effects of the implantation technique is to load the samples from the gas phase in thermodynamic equilibrium. Antonov *et al* (1980) loaded a $Pd_{0.80}Ag_{0.20}$ alloy with hydrogen at pressures up to 7 GPa. They found, however, no significant difference between the concentration dependence of T_c for the $Pd_{0.80}Ag_{0.20}$–H and the Pd–H system. On the basis of these results, Antonov *et al* (1980) and Ponyatovskii *et al* (1982) concluded that the high T_c-values found by Buckel and Stritzker (1973) and Stritzker (1974) are attributable to the specific properties of the metastable state of the thin hydride layer obtained during hydrogen implantation.

The available experimental and theoretical data on superconductivity in the Pd–Ag–H system appears to be a collection of apparently inconsistent results. In the rest of this paper, we shall try to bring some order in the available data. First we present the results on $Pd_{0.93}Ag_{0.07}$ hydrides, obtained in a diamond anvil cell (DAC). We analyse the measured T_c-values and their pressure dependence within the Allen–Dynes formalism, previously used for the Pd–H(D) system (Hemmes *et al* 1989a). Secondly, we discuss the influence of disorder on T_c. Finally, we performed thermodynamic calculations on the formation of Pd–Ag hydrides, in order to estimate the hydrogen concentration in our samples.

2. Experimental details

The diamond anvil cell (DAC), which is made entirely of a Be–Cu alloy (Berylco25), is mounted in an optical cryostat for use in the temperature range 2–300 K. The body of the cell contains a heat exchanger, which can be operated with liquid helium. With this facility we can cool the cell rapidly to liquid-helium temperature. The force on the diamonds can be changed continuously at all temperatures from the top of the cryostat. Details of the DAC and the cryogenic system have been described elsewhere (Hemmes *et al* 1989b).

In order to load the sample space with hydrogen, we built a small chamber around the diamond tips (for details see Hemmes *et al* (1989b)). The hydrogen is introduced into the chamber in gaseous form through a capillary. When filling the chamber with hydrogen the DAC is kept at a temperature just above the triple-point temperature of hydrogen (about 14 K). As a result the gas entering the chamber condenses at a density sufficient for further compression in a DAC. When the sample space is filled with liquid hydrogen, the temperature is lowered to solidify the hydrogen. Then sufficient force is applied to the diamonds to seal off the sample space. The DAC is heated to enable diffusion of hydrogen into the sample, which can be monitored by measuring the resistance of the sample. After the sample has been loaded with hydrogen, the DAC is cooled to measure T_c as a function of pressure.

The sample is made by deposition of a $Pd_{1-y}Ag_y$ film about 1000 Å thick on one of the diamonds. Photolithographic techniques are used to pattern the film. Details of the procedure have been given by Hemmes *et al* (1989b). The Pd–Ag films are deposited using a DC magnetron sputtering technique in an argon atmosphere. The base pressure of the vacuum system is about 10^{-7} mbar. During sputtering the argon pressure is kept at about 2×10^{-3} mbar. The substrate (a diamond from the DAC) has a temperature of about 600 K to improve sticking of the film and to reduce argon contamination. The

sputter target consists of a palladium disc with silver slices on top. The silver slices are spot welded to the palladium to improve electrical and thermal contact. The palladium-to-silver area ratio is chosen in such a way that the desired composition $Pd_{1-y}Ag_y$ is deposited on the substrate.

The composition of the Pd–Ag films is analysed using several techniques. The average composition is determined using an electron microprobe (EMP). The composition generally agrees very well with that expected from the sputter target. We also measured the resistance ratio (RRR) of the films. The silver concentration can be inferred from the RRR using the resistance data on bulk alloys. For the Pd–Ag alloy studied in this paper, we found that RRR = 2.53, corresponding to a silver concentration of 7.0 ± 0.5 at.% (according to the resistance data of Ricker and Pflüger (1966)). This is in excellent agreement with the value of 7.6 ± 0.5 at.% found from the EMP analysis.

Pd–Ag alloys are known to show an enrichment of the silver component at the surface (Miedema 1978). For thin films such as those used here, it is thus important to check the homogeneity of the sample. We therefore carried out x-ray photoelectron spectroscopy (XPS) measurements on the Pd–Ag films. On a film with an average silver concentration of 7 at.% we found at the surface a concentration of about 21 at.%. We then removed a layer of the film about 50 Å thick by sputtering with an argon ion gun. The silver concentration at the surface was then determined to be about 3 at.%. This is in good agreement with the available data in the literature (Mathieu and Landolt 1975, Slusser and Winograd 1979, Betz 1980, Betz *et al* 1980, Betz and Wehner 1983) which shows that, owing to preferential sputtering, the silver concentration at the surface is reduced below the bulk value. The 3 at.% found at the surface corresponds to a bulk value of about ~6 at.% (Betz *et al* 1980), in reasonable agreement with EMP and RRR results. The XPS results show that the surface segregation is limited to a very thin layer. This thin layer will have no significant influence on the properties of the film.

The technique used for electrical resistance measurements in a DAC has been described in detail by Hemmes *et al* (1989b). The main problem which had to be solved to measure the electrical resistance in the DAC was the insulation of the gasket. The gasket consists of a pre-pressed type 304 stainless steel foil of 100 μm thickness, with a hole 0.3 mm in diameter. An insulating Al_2O_3 layer 25 μm thick is deposited on the gasket by evaporation with an electron gun. A Kapton foil 25 μm thick is used as a soft interlayer between the hard and brittle Al_2O_3 and the sample.

The pressure is determined using the standard ruby fluorescence technique and the ruby pressure scale of Mao *et al* (1978).

3. Results

With the techniques described above, we have prepared $Pd_{0.93}Ag_{0.07}$ samples and loaded them with hydrogen and deuterium at pressures up to 8 GPa. The variation in the superconducting transition temperature with pressure is shown in figure 1. The transitions have a width varying from about 0.2 to 1 K. The transitions are, however, smooth and symmetric, allowing the T_c-values, defined by the midpoints of the transitions, to be determined with a typical accuracy of about 0.1 K. In the lowest data set (open triangles pointing upwards) the sample was loaded with hydrogen at a pressure of about 4.5 GPa. The pressure dependence of T_c was measured on lowering the pressure. When the pressure was lowered below about 3.5 GPa, electrical contact with the sample was lost. Contact could be restored by increasing the pressure. T_c was then measured up to
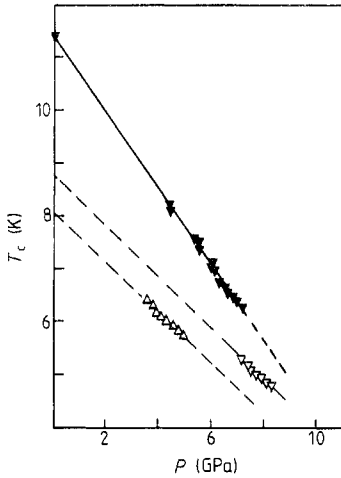
Figure 1. Superconducting transition temperature for $Pd_{0.93}Ag_{0.07}H_c$ ($\triangle$, lower hydrogen concentration; $\triangledown$, higher hydrogen concentration) and $Pd_{0.93}Ag_{0.07}D_c$ ($\blacktriangledown$) as a function of pressure.

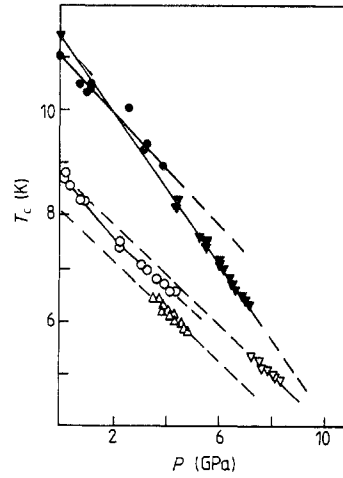**Figure 2.** Superconducting transition temperature as a function of pressure for $Pd_{0.93}Ag_{0.07}H_c$ ($\triangledown$, $\triangle$), $Pd_{0.93}Ag_{0.07}D_c$ ($\blacktriangledown$) (present results) and stoichiometric PdH ($\bigcirc$) and PdD ($\bullet$) (Hemmes *et al* 1989a).

5 GPa. The pressure dependences for increasing and decreasing pressure agree very well. At this point, we increased the pressure to about 8 GPa and heated the DAC. This resulted in a further uptake of hydrogen by the sample. This is clearly visible in T_c, which is shifted up by 0.7 K. The pressure dependence was then measured down to about 7 GPa (open triangles pointing downwards) where electrical contact was lost again and could not be restored. When the measured T_c-values are extrapolated to 0 GPa, we find that $T_c \simeq 8.1$ K for the lower hydrogen concentration and that $T_c \simeq 8.8$ K for the higher concentration. The slope of the lower curve is well determined. That of the curve with the higher hydrogen concentration is assumed to be the same as for the lower hydrogen concentration. The upper curve in figure 1 (full triangles) represents the data on $Pd_{0.93}Ag_{0.07}$ loaded with deuterium at a pressure of about 7.5 GPa. In this case we were able to measure T_c all the way to zero pressure. At 0 GPa, we find that $T_c = 11.4$ K, which is larger than the value of 11.05 K found for stoichiometric PdD (Hemmes *et al* 1989a).

In figure 2 the present results are shown together with the data on stoichiometric PdH and PdD (Hemmes *et al* 1989a). We observe that the slope for the $Pd_{0.93}Ag_{0.07}D_c$ curve is significantly larger than that of the others, which all have about the same slope. The difference arises because in this particular $Pd_{0.93}Ag_{0.07}$–D run the loading of the sample with deuterium resulted in loosening the film from the diamond. As discussed by Hemmes *et al* (1989a) the volume dependence of T_c for a free sample under hydrostatic pressure is related to the pressure dependence of T_c by

$$\partial(\ln T_c)/\partial(\ln V) = -B \, \partial(\ln T_c)/\partial P \tag{1}$$

while for a thin film sticking to a rigid substrate the sample can only respond with an uniaxial strain to a hydrostatic pressure (Landau and Lifshitz 1986) and consequently

$$\partial(\ln T_c)/\partial(\ln V) = -B[3(1 - \sigma)/1 + \sigma] \, \partial(\ln T_c)/\partial P \tag{2}$$

where B is the bulk modulus and σ Poisson's ratio. The volume dependence is the same
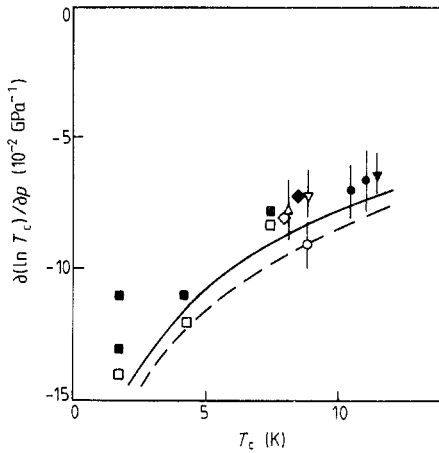
Figure 3. Pressure dependence of T_c for the hydrides ($\square$, $\diamond$, $\bigcirc$, $\triangledown$, $\triangle$) and deuterides ($\blacksquare$, $\blacklozenge$, $\bullet$, $\blacktriangledown$) of Pd–Ag and Pd, as a function of T_c: $\square$, $\blacksquare$, Pd–H(D), Schirber (1973); $\diamond$, $\blacklozenge$, Pd–H(D), Stritzker and Wühl (1978); $\bigcirc$, $\bullet$, Pd–H(D), Hemmes *et al* (1989a); $\triangledown$, $\triangle$, $\blacktriangledown$, $Pd_{0.93}Ag_{0.07}$–H(D), present results; – – –, theoretical result for $Pd_{0.93}Ag_{0.07}H_c$; ——, theoretical results for $Pd_{0.93}Ag_{0.07}D_c$. These curves are virtually the same as those for the Pd–H(D) system (for details see text and Hemmes *et al* (1989a)).

in the two cases. The only relevant quantity determining the difference in elastic response is Poisson's ratio σ. Since $\sigma \simeq 0.39$ for palladium as well as for PdH and silver (Hemmes *et al* 1989a, Loebisch 1966), we expect approximately the same value for the Pd–Ag–H(D) system. According to equations (1) and (2) the slope $\partial(\ln T_c)/\partial P$ for a 'free' sample is $3(1 - \sigma)/(1 + \sigma) \simeq 1.3$ times larger than that of a 'fixed' sample, in good agreement with the experimental data shown in figure 2.

Using the bulk modulus B for PdH of 160 GPa (Geerken *et al* 1982), equation (2) and $3(1 - \sigma)/(1 + \sigma)B \simeq 210$ GPa, we find, for the volume dependence of T_c, $\partial(\ln T_c)/\partial(\ln V) = 12.3$ at $T_c = 8.1$ K for the hydride with the lower hydrogen concentration and $\partial(\ln T_c)/\partial(\ln V) = 11.5$ at $T_c = 8.8$ K for the hydride with the higher hydrogen concentration. Using $B = 160$ GPa and equation (1), we find $\partial(\ln T_c)/\partial(\ln V) = 10.2$ at $T_c = 11.4$ K for the deuteride. For the pressure dependence of a 'free' sample we then find that $\partial(\ln T_c)/\partial P = -7.7 \times 10^{-2}$ GPa^{-1} at $T_c = 8.1$ K, $\partial(\ln T_c)/\partial P = -7.2 \times 10^{-2}$ GPa^{-1} at $T_c = 8.8$ K for the hydrides and $\partial(\ln T_c)/\partial P = -6.4 \times 10^{-2}$ GPa^{-1} at $T_c = 11.4$ K for the deuteride. These pressure dependences are plotted in figure 3 together with values for the Pd–H(D) system. The uncertainties in the experimental values are indicated by the vertical bars.

4. Discussion

4.1. T_c and its pressure dependence

We analyse the results on the superconducting transition temperature following the same approach previously used for the palladium hydrides (Hemmes *et al* 1989a). We start with the modification by Allen and Dynes (1975) of McMillan's (1968) T_c formula

$$T_c = (\omega_{\log}/1.20) \exp\{-1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)]\} \tag{3}$$

where $\omega_{\log}$ is a logarithmic average of the phonon frequencies, λ the electron–phonon coupling parameter and μ^* the Coulomb pseudopotential. λ can be written as the sum

of contributions from the metal (M) and hydrogen (deuterium) (Klein and Papa-constantopoulos 1976):

$$\lambda = \lambda_M + \lambda_{H(D)} \tag{4}$$

where λ_κ is given by (McMillan 1968, Klein and Papaconstantopoulos 1976)

$$\lambda_\kappa = \eta_\kappa/(m_\kappa \overline{\omega_\kappa^2}) \qquad (\kappa \equiv M, H(D)). \tag{5}$$

with m_κ the mass of the atom and $\overline{\omega_\kappa^2}$ the mean square of the phonon frequencies.

The 'electronic' factors η_κ of λ can be determined from band-structure calculations (McMillan 1968, Gaspari and Gyorffy 1972). The effect of the large zero-point motion (ZPM) of hydrogen (deuterium) on $\eta_{H(D)}$ is not taken into account in band-structure calculations. To incorporate the ZPM, Karakazov and Maksimov (1978) and Griessen and de Groot (1982) proposed that $\eta_{H(D)}$ should be multiplied by a Debye–Waller factor $f_{H(D)}$. This factor reduces the electron–phonon coupling strength. Because the role of the Debye–Waller factor is not crucial in the analysis of the present results, we refer to Hemmes *et al* (1989a) for the details.

Taking the logarithmic volume derivative of equation (3), we obtain

$$\partial(\ln T_c)/\partial(\ln V) = -\gamma_{\log} + g(\lambda)\,\partial(\ln \lambda)/\partial(\ln V) \tag{6}$$

with $\gamma_{\log} = -\partial(\ln \omega_{\log})\partial(\ln V)$ and $g(\lambda) = 1.04\lambda(1 + 0.38\mu^*)/[\lambda - \mu^*(1 + 0.62\lambda)]^2$. We treat μ^* as a constant since we expect it to have only a small volume dependence compared with λ. Using equation (4), the volume dependence of λ can be expressed as

$$\partial(\ln \lambda)/\partial(\ln V) = (\lambda_M/\lambda)\,\partial(\ln \lambda_M)/\partial(\ln V) + (\lambda_{H(D)}/\lambda)\partial(\ln \lambda_{H(D)})/\partial(\ln V). \tag{7}$$

For the volume dependence of λ_M and $\lambda_{H(D)}$, we find that

$$\partial(\ln \lambda_M)/\partial(\ln V) = 2\gamma_M^\omega - \gamma_M^\eta \tag{8a}$$

$$\partial(\ln \lambda_{H(D)})/\partial(\ln V) = 2\gamma_{H(D)}^\omega - \gamma_{H(D)}^\eta - \gamma_{H(D)}^f \tag{8b}$$

where the γ-values are defined by

$$2\gamma_\kappa^\omega = -\partial[\ln(m_\kappa \overline{\omega_\kappa^2})]/\partial(\ln V) \tag{9a}$$

$$\gamma_\kappa^\eta = -\partial(\ln \eta_\kappa)/\partial(\ln V) \qquad (\kappa \equiv M, H(D)) \tag{9b}$$

$$\gamma_{H(D)}^f = -\partial(\ln f_{H(D)})/\partial \ln V). \tag{9c}$$

In order to calculate T_c and its pressure dependence, a large number of parameters are needed. These parameters are the acoustic and optic phonon frequencies ω_M and $\omega_{H(D)}$ and their volume dependences γ_M^ω and $\gamma_{H(D)}^\omega$, the electronic parts η_M and $\eta_{H(D)}$ of the electron–phonon coupling parameter λ_M and $\lambda_{H(D)}$ for the metal and the hydrogen (deuterium) and their volume dependences γ_M^η and $\gamma_{H(D)}^\eta$, the Debye–Waller factor $f_{H(D)}$ and its volume dependence $\gamma_{H(D)}^f$, and the elastic constants σ and B to compare the experimental pressure dependence with the theoretical volume dependence of T_c. For stoichiometric PdH and PdD, all these quantities could be determined from available experimental data or could be calculated (Hemmes *et al* 1989a). Unfortunately the Pd–Ag–H(D) system has not been studied in as great detail as the Pd–H(D) system. We have therefore to estimate some of the parameters, as they are not available from literate.

Table 1. Parameters needed to calculate T_c and $\partial(\ln T_c)/\partial(\ln V)$ from equations (3) and (6). The values for λ_H and λ_D are those that reproduce the experimental T_c-values at zero pressure. The other parameters are obtained as discussed in the text.

κ	ω_κ (K)	λ_κ	γ^ω_κ	λ^η_κ	γ^f_κ	μ^*
M	230	0.175	2.5	3.4	—	
H	728	0.3734	3.5	−1.22	0.87	0.085
D	485	0.4757	3.5	−1.22	0.65	

The phonon frequencies can be obtained from neutron scattering data. The neutron scattering results of Chowdhury and Ross (1973) and Fratzl *et al* (1986) show no significant changes in the phonon frequencies compared with the Pd–H system. For the $Pd_{0.93}Ag_{0.07}$–H(D) system studied here, we use therefore the same phonon frequencies as for the Pd–H(D) system. The volume dependence of the phonon frequencies is not well known. Because of the lack of experimental data we take the same volume dependence as for the Pd–H(D) system. For the $Pd_{0.93}Ag_{0.07}$–H(D) system this is probably a reasonable assssumption. Similarly for the Debye–Waller factor, as $f_{H(D)}$ depends on the phonon frequencies and the lattice parameter (Griessen and De Groot 1982), one expects that the Debye–Waller factor and its volume dependence will be approximately the same for $Pd_{0.93}Ag_{0.07}$–H(D) and Pd–H(D).

The electronic factors η_M and $\eta_{H(D)}$ of the electron–phonon coupling parameter λ have been calculated by Papaconstantopoulos *et al* (1979). In these calculations the virtual-crystal approximation was used to take the substantial disorder into account. As there were some doubts about the validity of the approximations used, Laufer and Papaconstantopoulos (1985, 1986) recalculated later the η-values using the coherent-potential approximation for the disorder. For silver concentrations up to 30 at.% they found the same values for the η-values. For 7 at.% Ag the value of η_M is the same as for pure PdH; the value of $\eta_{H(D)}$ is somewhat larger, mainly as a result of the increased s-like density of states, at the hydrogen sites, at the Fermi level. For the volume dependence of the η-values there are no data available. However, as the silver content is low and the electronic structure of the Pd–Ag hydrides is very similar to that of the palladium hydrides, we expect the volume dependence to be similar to that of PdH. Therefore we use the calculated values for PdH (Hemmes *et al* 1989a).

As already discussed in § 3, Poisson's ratio σ for $Pd_{0.93}Ag_{0.07}$–H is estimated to be about 0.39. Since the bulk modulus of $Pd_{0.93}Ag_{0.07}$ is approximately the same as for palladium (Belmani *et al* 1966, Walker *et al* 1970), we use the same bulk modulus for $Pd_{0.93}Ag_{0.07}$–H(D) as for Pd–H(D).

The values of the parameters listed above are summarised in table 1. Using equations (3)–(5) and the parameters from table 1, we estimated $\eta_{H(D)}$ from the measured T_c. With this $\eta_{H(D)}$, equation (6) and the parameters from table 1, we calculated the volume dependence of T_c. We find for the hydrides that $\partial(\ln T_c)/\partial(\ln V) = 14.4$ at $T_c = 8.1$ K and that $\partial(\ln T_c)/\partial(\ln V) = 14.0$ at $T_c = 8.8$ K. For the deuteride we find that $\partial(\ln T_c)/\partial(\ln V) = 11.5$ at $T_c = 11.4$ K. The calculated volume dependences are in reasonable agreement with those determined from the experimental pressure dependence of T_c in § 3.

Most parameters are fairly insensitive to the hydrogen concentration in the region where superconductivity occurs. The only parameter that depends strongly on the

hydrogen concentration is $\eta_{H(D)}$ and its volume dependence $\gamma^{\eta}_{H(D)}$. However, as shown by Hemmes *et al* (1989a), $\gamma^{\eta}_{H(D)} \propto 1/\eta_{H(D)}$. As $\gamma^{\eta}_{H(D)}$ appears only as a product with $\lambda_{H(D)}$, its concentration dependence is cancelled by that of $\lambda_{H(D)}$. Consequently the concentration dependence of both T_c and $\partial(\ln T_c)/\partial(\ln V)$ is determined by the concentration dependence of $\eta_{H(D)}$. Equations (3) and (6) can now be used as parametric expressions for T_c and $\partial(\ln T_c)/\partial(\ln V)$, with $\eta_{H(D)}$ (or $\lambda_{H(D)}$) as parameter. These equations together with equation (1) define a curve in the $\partial(\ln T_c)/\partial P$–$T_c$ plane. With the parameters in table 1 we calculated the curves of $\partial(\ln T_c)/\partial P$ against T_c for the hydride and the deuteride of $Pd_{0.93}Ag_{0.07}$. Because most parameters assume the same value as in PdH and PdD, these curves are virtually the same as for the Pd–H(D) system (Hemmes *et al* 1989a). The results are plotted in figure 3 together with the available experimental data on the Pd–Ag–H(D) and Pd–H(D) systems.

4.2. Influence of disorder on T_c

As already mentioned in § 1, the side effects of the implantation technique on T_c are not clear. Antonov *et al* (1980) suggested that the metastable state of the hydride and the induced lattice imperfections increase T_c. This view seems to be supported by the occurrence of superconductivity in palladium films irradiated with α-particles (Stritzker 1978, 1979). On the contrary there is no apparent influence on T_c for PdH and PdD (Stritzker and Buckel 1972, Ginodman and Zherikhina 1980, Hemmes *et al* 1989a).

Belitz (1987) showed recently that, within a jellium model, the disorder dependence of T_c is determined by competition of the repulsive Coulomb interactions and the attractive phonon-mediated electron–electron interactions. The disorder dependence of T_c changes sign as a function of T_c. For 'low' T_c-values, T_c increases and, for 'high' T_c-values, it decreases with increasing disorder. In general the details of the band structure and phonon spectrum, which are neglected in Belitz's calculations, can be important in real maerials. However, we expect them to be of minor importance for the Pd–Ag–H(D) system, since there is no pronounced structure in the electron density-of-states curve at the Fermi level and no particular phonon modes which are likely to be strongly disorder dependent.

From a comparison of the data of PdH with the results presented in figure 2 of Belitz (1987) we find that they fall in the region where the disorder dependence of T_c changes sign and subsequently is small. This accounts for the absence of disorder effects on the T_c of implanted PdH samples. The enhancement of superconductivity in irradiated 'low'-T_c materials such as aluminium and indium (Hofmann *et al* 1981, Bernas and Nedellec 1981) is also consistent with the positive disorder dependence in Belitz's (1987) calculations. The occurrence of superconductivity in α-irradiated palladium films (Stritzker 1978, 1979) also fits into the picture, although in this case the suppression of paramagnons is probably of major importance. From the model discussed above, we would expect a decrease in T_c for 'high'-T_c materials when disorder is introduced. As a consequence the T_c-values found in implanted samples should be lower than in samples loaded by methods that introduce less disorder.

4.2. Formation of Pd–Ag hydrides

Because of the small size of the samples used in a DAC, the hydrogen concentration cannot be determined experimentally. We therefore use thermodynamic calculations of the formation of Pd–Ag hydrides to estimate the hydrogen contents of our samples.

    For the calculation of the pressure–composition isotherms we use a multi-site lattice-gas model (Griessen and Driessen 1984, Griessen 1986). We assume the hydrogen occupies the octahedral interstitial sites in the FCC lattice of $Pd_{1-y}Ag_y$ (as in pure palladium) and that there is at most one hydrogen atom at a given site. We further assume that the six metal atoms surrounding the octahedral interstitial site determine its properties. Then there are seven different sites: Pd_6, Pd_5Ag_1, . . . , Pd_1Ag_5 and Ag_6, determined by the number of palladium and silver atoms. The fraction x_j ($0 \le j \le 6$) of occupied sites, with energy ε_j, is given by a Fermi–Dirac distribution (Kirchheim *et al* 1982, Griessen 1983, 1986)

$$x_j = [\exp\{[\varepsilon_j + \varepsilon(T) + f(c, T) + p\bar{V}_H - \mu_H]/RT\} + 1]^{-1} \qquad (10)$$

where $f(c, T)$ describes the dependence of the site energy on the total hydrogen concentration c, $\varepsilon(T)$ describes the temperature dependence of the site energy and is mainly determined by the vibrations of the hydrogen in the metal, μ_H is the chemical potential of the hydrogen in the metal, $\bar{V}_H$ is the molar volume of hydrogen in the metal, p is the pressure, R is the gas constant and T is the absolute temperature. The total concentration c is defined as the fraction of available interstitial sites with octahedral symmetry that is occupied by hydrogen atoms. In a FCC lattice the number of interstitial sites with octahedral symmetry is equal to the number of metal atoms; so $c = [H]/[M]$. At thermodynamic equilibrium the chemical potential μ_H of the hydrogen atoms occupying interstitial sites of type j in the alloy is related to the chemical potential of the hydrogen gas surrounding the sample by μ_{H_2} $(p, T) = 2\mu_H(\varepsilon_j, p, T)$. If g_j is the fraction of interstitial sites with energy ε_j, the total concentration c of hydrogen is given by

$$c = \sum_j g_j x_j(\varepsilon_j, c, p, T, \mu_H). \qquad (11)$$

Equation (11) defines an implicit relation for c, which can be solved numerically. Details of the calculations have been published elsewhere (Hemmes *et al* 1989c).

    The thermodynamic calculations are able to reproduce, with reasonable accuracy, all available low- and high-pressure data on the Pd–Ag–H system. As an example the calculated isotherms for $Pd_{0.50}Ag_{0.50}H_c$ are shown in Figure 4. There is a good agreement with the experimental data of Ponyatovskii *et al* (1984). We also calculated pressure–composition isotherms for several Pd–Ag alloys. Figure 5 shows the 400 K isotherms for a number of silver concentrations. We see that above 10^5 Pa, the hydrogen concentration decreases as the silver content increases. The behaviour at lower pressures is consistent with the low-pressure results of Yoshihara and McLellan (1985). For the alloys with higher silver contents, stoichiometry cannot be reached as the isotherms exhibit a turnover behaviour around 70 GPa when $2\bar{V}_H = \bar{V}_{H_2}$, where $\bar{V}_{H_2}$ is the molar volume of molecular hydrogen (see also Hemmes *et al* (1989c)). The undulations, present in some of the isotherms above 10 GPa, are due to the gradual filling of the silver-rich interstitial sites. In figure 6 we have plotted the hydrogen concentration at 8 GPa, the loading pressure of our samples, as a function of the palladium content of the alloys. At 8 GPa, the hydrogen concentration is not much larger than the palladium concentration. From these isotherms we estimate a hydrogen concentration of about 98 at.% for the $Pd_{0.93}Ag_{0.07}$ alloy loaded at about 8 GPa. Because of the similarity of the Pd–H and the Pd–D systems we expect approximately the same concentration for the deuteride. To increase the hydrogen concentration significantly above the palladium contents of the alloys, especially for higher silver contents, pressures well above 10 GPa are needed.
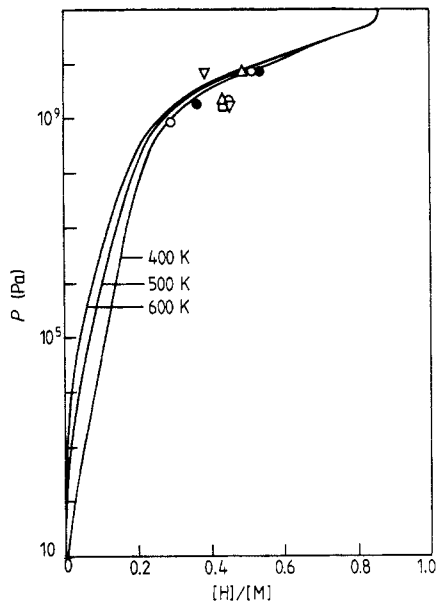
Figure 4. Calculated pressure–composition isotherms (——), at $T = 400, 500$ and 600 K, for the $Pd_{0.50}Ag_{0.50}H_c$ system. The experimental data ($\square$, 373 K; $\triangledown$, 473 K; $\triangle$, 573 K; $\bigcirc$, 623 K; $\bullet$, 673 K) is from Ponyatovskii *et al* (1984).
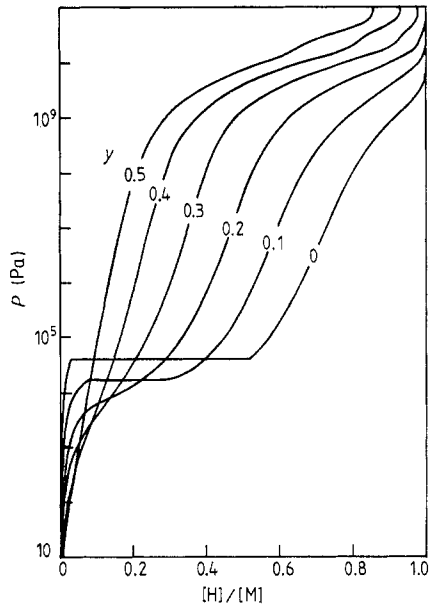
Figure 5. $Pd_{1-y}Ag_yH_c$ pressure–composition isotherms at $T = 400$ K for $y = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5, calculated by means of a multi-site model for hydrogen in disordered alloys (Griessen 1986, Feenstra *et al* 1986, Hemmes *et al* 1989c).
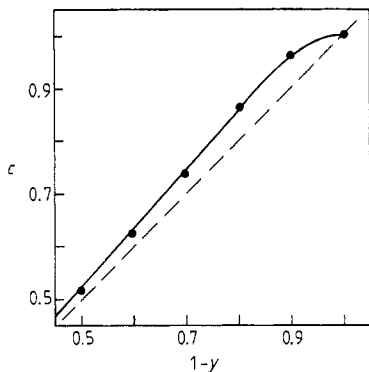

Figure 6. Hydrogen concentration $c = [H]/[M]$ at 8 GPa and $T = 400$ K for the $Pd_{1-y}Ag_y$–H system as a function of the palladium concentration $1 - y$: ---, $c = 1 - y$.

From the calculated pressure–composition isotherms, we estimate that a loading pressure of about 20 GPa is needed to synthesise stoichiometric $Pd_{0.93}Ag_{0.07}H_1$.

Using the known concentration dependence of T_c for PdH_c and PdD_c, the hydrogen (deuterium) concentration c and the experimental T_c at zero pressure, we can estimate T_c for stoichiometric $Pd_{0.93}Ag_{0.07}H_1$ and $Pd_{0.93}Ag_{0.07}D_1$. The concentration dependence of T_c at $c \simeq 1$ for both PdH_c and PdD_c is about 0.7 K (at.% H(D))$^{-1}$ (Ginodman and Zherikhina 1980). For the samples loaded at about 8 GPa we have $T_c(0) \simeq 9$ K at $c \simeq$

98 at. % for the hydride and $T_c(0) \simeq 11.4$ K at $c \simeq 94$ at. % for the deuteride. From this we estimate that $T_c \simeq 10.5$ K for $Pd_{0.93}Ag_{0.07}H_1$ and $T_c \simeq 13$ K for $Pd_{0.93}Ag_{0.07}D_1$, in reasonable agreement with the results for the implanted Pd–Ag hydrides and deuterides (Buckel and Stritzker 1973, Stritzker 1974). This suggests that there is only a small influence of disorder for these materials. This is consistent with the disorder dependence of T_c discussed above, because T_c falls in the region where the disorder dependence of T_c changes sign (Belitz 1987) and subsequently is small.

5. Conclusions

We have synthesised hydrides of $Pd_{0.93}Ag_{0.07}$ at pressures up to 8 GPa in a DAC and measured *in situ* the pressure dependence of the superconducting transition temperature. The measured T_c-values and their pressure dependence are well described within the Allen–Dynes formalism, previously used for the Pd–H(D) system. This supports the correctness of the theoretical approach and in part the results of Papaconstantopoulos *et al* (1979). Thermodynamic calculations of the formation of Pd–Ag hydrides show that pressures well over 10 GPa are needed to approach stoichiometric hydrogen concentrations. We believe that refinements of our experimental techniques will make it possible to load alloys at significantly higher hydrogen pressures. The agreement that we find between T_c for $Pd_{0.93}Ag_{0.07}H_1(D_1)$ and implantation results (Buckel and Stritzker 1973, Stritzker 1974) is consistent with the discussed disorder dependence of T_c. The bulk of the experimental evidence supports the idea that higher T_c-values than found in the implantation measurement should be possible. Only the data of Antonov *et al* (1980) on $Pd_{0.80}Ag_{0.20}H_c$ are not in agreement with the picture presented in this paper. At this moment there seems no way in which these results can be reconciled with the rest of the data.

Acknowledgments

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