

Influence of hydrogen on the thermoelectric power of palladium alloyed with neighbouring elements: I. Pd/Ru/H and Pd/Rh/H alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 3583

(<http://iopscience.iop.org/0953-8984/15/21/307>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 09:57

Please note that [terms and conditions apply](#).

Influence of hydrogen on the thermoelectric power of palladium alloyed with neighbouring elements: I. Pd/Ru/H and Pd/Rh/H alloys

A W Szafranski

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52,
01-224 Warsaw, Poland

E-mail: aws@ichf.edu.pl

Received 3 January 2003

Published 19 May 2003

Online at stacks.iop.org/JPhysCM/15/3583

Abstract

Pd/Ru and Pd/Rh alloys have been loaded with hydrogen in high-pressure conditions. The resulting hydrogen contents were close to the stoichiometric composition, $H/(Pd + Me) = 1$. Lower hydrogen contents have been obtained by successive partial desorptions. The thermoelectric power and electrical resistance of one- and two-phase alloys have been measured simultaneously in the temperature range between 80 and 300 K. A Nordheim–Gorter type correlation of the two quantities has been observed in many cases and the partial thermopowers corresponding to electron–phonon scattering and lattice disorder could be determined. The observed anomalous behaviour of the total and partial thermopowers is attributed to virtual bound states of ruthenium or rhodium.

1. Introduction

The electronic structure of palladium alloys and their hydrides has been intensively experimentally and theoretically studied in the past (see [1–3]). The conclusion was that the rigid band model is not applicable to these systems. Nevertheless, some conclusions derived from this model appeared to be right. The elements added to Pd standing in the periodic table to the right of it (silver) and hydrogen act as electron donors, while those standing to the left (rhodium) act as electron acceptors. The essential net result of the alloying is a shift of the Fermi level towards either higher or lower energies. In the former case (the best examples are Pd–Ag and Pd–H alloys) the empty 4d states are filled up and the density of states is strongly reduced. Thus, many of the physical properties (e.g. magnetic susceptibility, electronic specific heat, electrical conductivity, thermoelectric power (TEP)) of the silver-rich Pd/Ag alloys and of the Pd hydride are quite different as compared to those of pure palladium.

A flat low-temperature Kondo-like minimum has been found in the case of hydrogenated palladium, PdH_{~0.6}, alloyed with neighbouring elements in the 1.5–40 K range (Pd/Ru [4],

Pd/Ir, Pd/Rh [5]). Its position in the temperature scale and depth are dependent on alloy composition and hydrogen content. The phenomenon was attributed to magnetic moments being localized on solute atoms. The minimum tended to vanish when hydrogen content increased, in agreement with a prediction based on the *virtual bound state/localized magnetic moment* (VBS/LMM) model proposed by Wicke and Fröhlich [6].

The band structure of stoichiometric PdH has some similarities with silver in the following aspects:

- (i) the Fermi level is located above the top of the 4d states where the density of 5s–5p states is low and
- (ii) the Fermi surface is approximately a sphere with ‘necks’ touching the Brillouin zone in some directions of k -space.

On the other hand, the presence of the solute VBS can significantly affect the TEP of palladium hydride as this physical quantity is very sensitive to details of the electronic structure. In this paper we check the influence of additions of Ru and Rh, elements standing to the left of palladium, on the TEP of β -phase palladium hydride (PdH_c , $0.6 \leq c \leq 1$). Recently a marked influence of the additions of metals standing in the table of elements to the left of nickel (V, Cr, Fe, Co) on the TEP of nickel hydride, an analogue of the noble metal copper, was reported [7, 8].

2. Experimental details

The palladium alloys (0.6 and 2 at.% Ru; 2.7, 5 and 10 at.% Rh) in the form of small foil samples ($10 \times 1 \times 0.02 \text{ mm}^3$) have been exposed at room temperature to gaseous hydrogen compressed to 0.9 GPa for 3–5 days. Thereafter the pressure chamber was cooled down to about 170 K and the pressure released. Such a procedure greatly prevents hydrogen desorption. The resulting hydrogen contents, $c \equiv \text{H}/(\text{Pd} + \text{Me})$, were close to a stoichiometric value of unity. The TEP, S , and electrical resistance, r , of the hydride samples, as received after hydrogen loading (labelled ‘1’ on figures below) and after successive partial hydrogen desorptions (labelled ‘2’, ‘3’ etc), have been measured simultaneously in the temperature range between 80 and 300 K. The hydrogen contents were measured directly either with the use of a mass-spectrometer or were estimated from electrical resistance, in the latter case based on the previously measured $r(c, T)$ relationships. c -values lower than about 0.6 correspond to the two-phase composition, $\alpha\text{-(PdMe)H}_{c_\alpha} + \beta\text{-(PdMe)H}_{c_\beta}$, where $c_\alpha \approx 0.03\text{--}0.05$ and $c_\beta \approx 0.5\text{--}0.6$. More experimental details can be found in [7] and [9].

Separate measurements of electrical resistance of the hydrogenated alloys have been performed in the low-temperature region (1.5–300 K).

3. Results and discussion

3.1. Thermoelectric power

The temperature dependence of the TEP of selected hydrogenated Pd/Ru and Pd/Rh alloys is shown in figures 1–3 and 5. The curves labelled ‘0’ refer to the hydrogen-free alloys. The first few runs refer to a β -phase composition and the other to a two-phase, $\alpha + \beta$, mixture. The thermopower of the two-phase mixture is approximately equal to a weighted average of thermopowers corresponding to the two phases with weights proportional to their contents (see e.g. [9]). Thus if, at temperature T' , $S(T', \alpha) = S(T', \beta)$, then $S(T', \alpha + \beta) = S(T', \alpha) = S(T', \beta)$ for all hydrogen contents corresponding to the two-phase range. This means that the $S(T, \alpha + \beta)$ -curves should cross each other at T' . This is clearly seen in the case of the

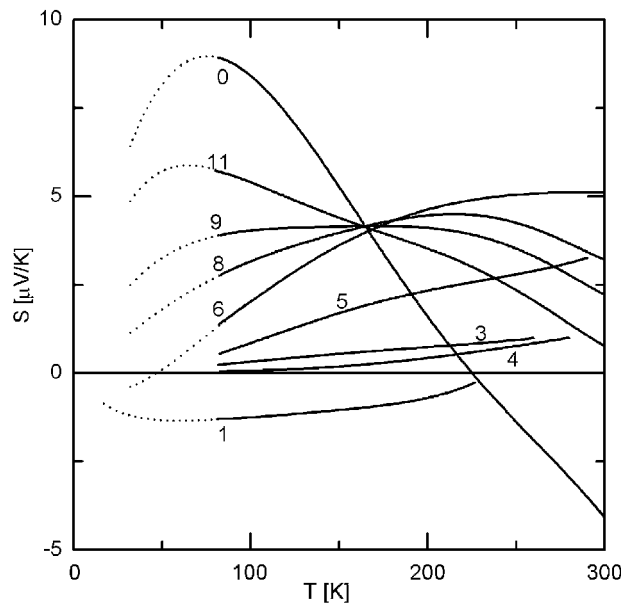


Figure 1. Temperature dependence of TEP of $\text{Pd}_{0.994}\text{Ru}_{0.006}\text{H}_c$ alloys; 1 — $c = 0.98$, 4 — $c = 0.75$, 6 — $c = 0.55$, 0 — $c = 0$. Hypothetical trends below 80 K are denoted by dots.

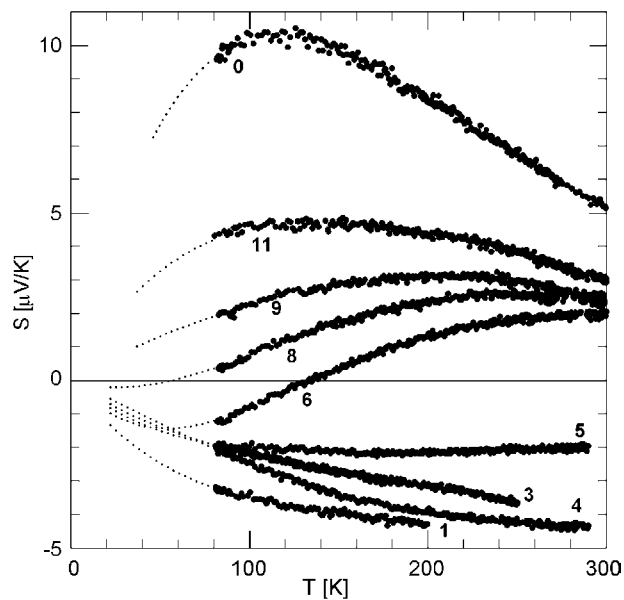


Figure 2. Temperature dependence of TEP of $\text{Pd}_{0.98}\text{Ru}_{0.02}\text{H}_c$ alloys; 1 — $c = 0.98$, 4 — $c = 0.75$, 6 — $c = 0.55$, 0 — $c = 0$. Hypothetical trends below 80 K denoted by dots.

$\text{Pd}_{0.994}\text{Ru}_{0.006}\text{H}_c$ alloys for $0 \leq c \leq 0.55$ (runs 6–11 and 0 in figure 1), where $T' = 165$ K (for $\text{Pd}_{0.98}\text{Ru}_{0.02}\text{H}_c$ and PdH_c alloy systems T' is equal to ~ 360 K (figure 2) and ~ 80 K [9], respectively).

A maximum in the $S(T)$ relationship of the hydrogen-free alloys appears at low temperatures. In the case of pure palladium it is located close to 50 K and is attributed to

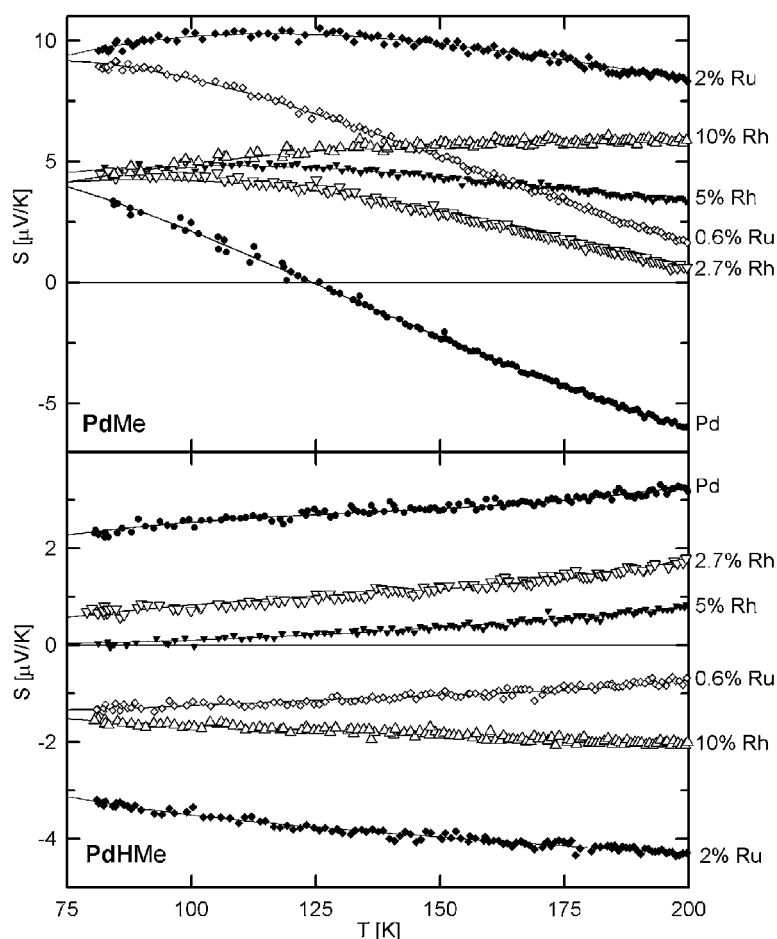


Figure 3. Temperature dependence of TEP of (a) hydrogen-free and (b) highly hydrogenated ($0.94 \leq c \leq 0.98$) Pd [8], PdRu and PdRh.

the phonon drag (see e.g. [10]). It shifts to higher temperatures upon addition of the second element (figure 3(a)). The character of the $S(T)$ relationships changes qualitatively when the alloys are transformed to the stoichiometric hydride phase (figure 3). The sign of the TEP is usually reversed. The low-temperature maximum is not present and the $S(T)$ relationship is monotonic within the temperature range measured.

Values of the TEP corresponding to 200 K, plotted as a function of hydrogen content, $S(c)$, are shown in figures 4 and 6. The $S(c)$ relationship for PdH_c alloys [9] is given for comparison.

3.1.1. Pd/Ru/H. A pronounced effect of the addition of ruthenium to both pure palladium and palladium hydride could be noted. TEP, equal to -6 and $+4.5 \mu\text{V K}^{-1}$ at 200 K, for pure Pd and PdH_{0.9}, respectively, changes its sign upon the addition of 0.6 at.% of ruthenium (figure 4). In the case of hydrogen-free alloys this effect was attributed [11] to virtual bound states of ruthenium formed close to the Fermi level [6] (see figure 7(a)). A model proposed by Wicke and Fröhlich [6] assumed splitting of the Ru VBS into two sub-VBSs with opposite spin direction resulting from the strong reduction of the electron density of states at the Fermi level

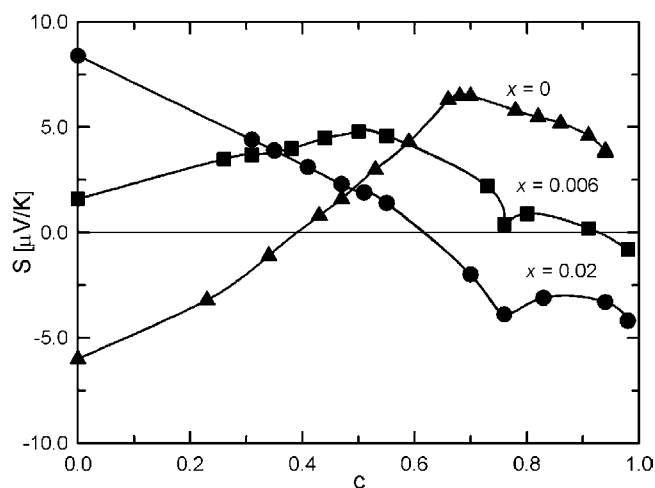


Figure 4. TEP of $\text{Pd}_{1-x}\text{Ru}_x\text{H}_c$ alloys at 200 K; the data for PdH_c [8] are given for comparison.

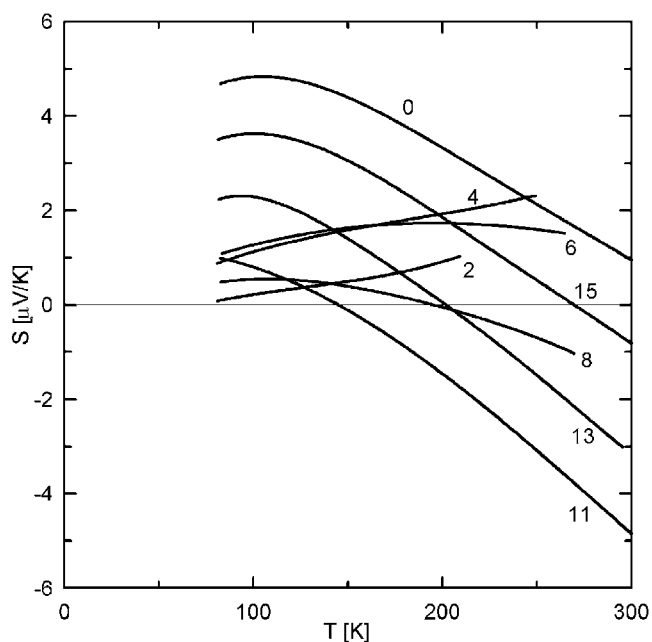


Figure 5. Temperature dependence of TEP of $\text{Pd}_{0.95}\text{Rh}_{0.05}\text{H}_c$ alloys; 2 — $c = 0.97$, 4 — $c = 0.93$, 8 — $c = 0.82$, 11 — $c = 0.55$, 0 — $c = 0$.

upon β -phase formation (figure 7(b)). The lower, spin-down sub-VBS is filled up but the upper spin-up one, which is only partially filled, gives rise to localized magnetic moments. Further increase of the hydrogen content (so the Fermi energy as well) leads to a gradual filling of these spin-up states. Close to the stoichiometric composition, PdHRu , the Fermi level is expected to be located in energy high enough for these spin-up states to be filled up (figure 7(c)). This model could explain anomalies observed in specific heat, magnetic susceptibility [12] and the Kondo effect in electrical resistance [4] for medium hydrogen contents, as well as the vanishing of these anomalous phenomena for higher hydrogen concentrations. The present results for

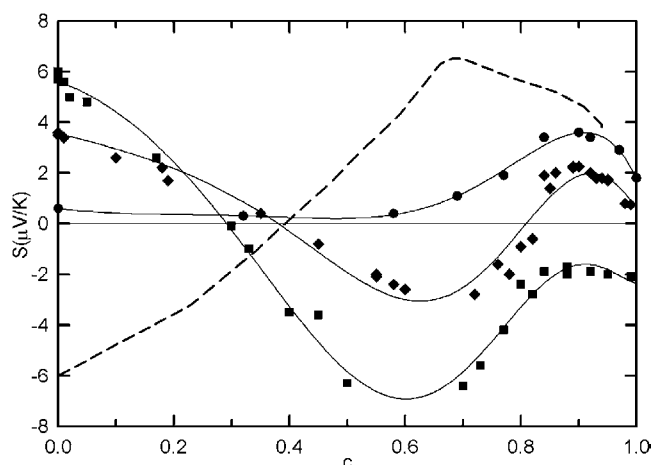


Figure 6. Thermoelectric power, TEP, of $\text{Pd}_{1-x}\text{Rh}_x\text{H}_c$ alloys at 200 K. ●— $x = 0.027$, ◆— $x = 0.05$, ■— $x = 0.10$; dashed curve— PdH_c [8]. The solid curves have been introduced to guide the eye.

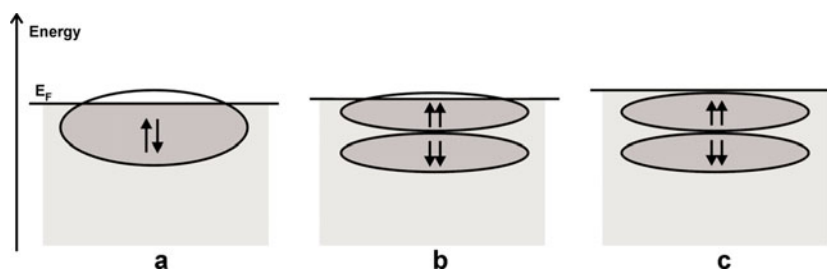


Figure 7. VBS/LMM model of Wicke and Fröhlich [6] for PdRu/H alloys. (This figure is in colour only in the electronic version)

$\text{Pd}_{0.98}\text{Ru}_{0.02}\text{H}_c$ alloys seem to support this model—the shape of the $S(T)$ relationship for $c \approx 0.55$ (see run 6 in figure 2) indicates the existence of a minimum located well below 80 K (the corresponding resistance minimum was detected at 35 K [4]). For $c \approx 0.7$ (run 5) TEP is negative with a very flat minimum at ~ 150 K, and it is nearly constant at higher temperatures. At higher hydrogen contents the minimum is absent (runs 1–4). The behaviour of the TEP of $\text{Pd}_{0.994}\text{Ru}_{0.006}\text{H}_c$ alloys is somewhat similar but the flat minimum is preserved up to highest c values (figure 1). The nature of this flat minimum is not clear, as no anomaly has been detected in the temperature dependence of the electrical resistance in the highly hydrogenated $\text{Pd}_{0.994}\text{Ru}_{0.006}$ and $\text{Pd}_{0.98}\text{Ru}_{0.02}$ alloys down to 3.9 K (where a transition to a superconducting state occurred) and to 1.6 K, respectively.

The $|dS/dx|$ quantity is large for H-free alloys ($dS/dx \approx +10 \mu\text{V K}^{-1}/\text{at.}\% \text{ Ru}$ at 200 K) but in the case of PdRu hydride it is markedly lower. Nevertheless, the corresponding value, $dS/dx \approx -3.5 \mu\text{V K}^{-1}/\text{at.}\% \text{ Ru}$ for $c \sim 0.9$, is one order of magnitude higher as compared to that corresponding to Pd/Rh/H (see figure 6) and other solutes [9].

The TEP of the two-phase alloy changes monotonically when plotted versus hydrogen content. However, in the β -phase region this change is not monotonic and a maximum (located at $c \approx 0.85$) following a minimum (located at $c \approx 0.75$), is observed (figure 4). Relationships analogous in shape, S versus p_{H_2} , have been derived from the high pressure measurements [5].

This indicates that the kinks seen for $c \approx 0.75$ are real. This anomalous behaviour seems to be due to a presence of ruthenium atoms, since no such kink could be detected in the case of the Pd/H system.

3.1.2. Pd/Rh/H. About 2.7 at.% rhodium is enough for the TEP sign change of both the pure alloy and the hydride ($c \approx 0.6$). A low-temperature maximum can be seen in hydrogen-free **PdRh** alloys and in their **PdH_{0.6}Rh** hydrides as well (see figure 5). This maximum shifts to higher temperatures and diminishes with further increase of hydrogen content. Finally, only a monotonic increase of TEP can be observed (see also figure 3). In contrast to the case of pure palladium and perhaps the most dilute **PdRu** alloy, the maximum cannot be attributed to phonon drag because of the high lattice disorder (i.e. the disorder due to random distribution of (i) Pd and Ru or Rh atoms in the fcc lattice and (ii) H atoms in the hydrogen sub-lattice unless the latter is fully occupied).

There is no evidence for a low-temperature minimum in the $S(T)$ relationship. This is in contrast with a weak resistive Kondo effect detected in this alloy system and attributed to the rhodium VBS [5]. The weakness of this effect is presumably due to the lower position of the Rh VBS with respect to the Fermi level as compared to the case of ruthenium (see [6]). The minimum was located at a lower temperature (~ 10 K) than it was in the case of Pd/Ru/H. That is why the influence of the Kondo scattering on the TEP behaviour above 80 K might be negligibly small.

The relationship between TEP and hydrogen content appears not to be monotonic in the β -phase region (figure 6). A similar non-monotonic behaviour has been observed in the high-pressure studies [5]. The effect of rhodium on the TEP of β -**PdH_c** at 200 K is highest for $c \approx 0.6$ and comparable to that for the Pd/Ru/H system.

3.2. Electrical resistance

The behaviour of the electrical resistance of nearly all hydrogenated Pd-rich alloys is similar to that observed in the case of the PdH_c alloy system [9] (see figure 8 for Pd_{0.95}Rh_{0.05}H_c alloys, as an example). At a given temperature the electrical resistance attains maximal values for medium hydrogen contents where the disorder of the hydrogen sublattice is high due to the random occupancy of the available interstitial (octahedral) sites.

A position, T_m , of the electrical resistance minimum, derived from low-temperature $r(T)$ measurements, is shown in figure 9. The presence of the minimum is interpreted as a Kondo effect due to the LMM of ruthenium or rhodium, induced by the absorbed hydrogen. The minimum depth decreases gradually as the hydrogen content tends to stoichiometry. In the case of β -Pd/Rh/H alloys T_m appears to be a non monotonic function of hydrogen content.

3.3. Correlation between thermoelectric power and electrical resistance

A correlation has been observed (see figure 10 as an example) between the TEP, S , and electrical resistance, r , of the Nordheim–Gorter type (see [13], see also [9]),

$$S(T)/T = A + B/r(T), \quad (1)$$

and the partial diffusion thermopowers, S_{ph} and S_{dis} , corresponding to electron–phonon scattering and lattice disorder, respectively, could be determined. The essential assumption was the additivity of resistivities coming from the two electron scattering types, $r(T) = r_{dis} + r_{ph}(T)$. So $S = (r_{dis}/r)S_{dis} + (r_{ph}/r)S_{ph}$, where the partial thermopowers are defined as [14]

$$S_i = \frac{\pi^2 k^2}{3|e|E_F} \left(\frac{d \ln r_i}{d \ln E} \right)_{E_F} T \equiv a_i T, \quad i = \text{dis or ph.} \quad (2)$$

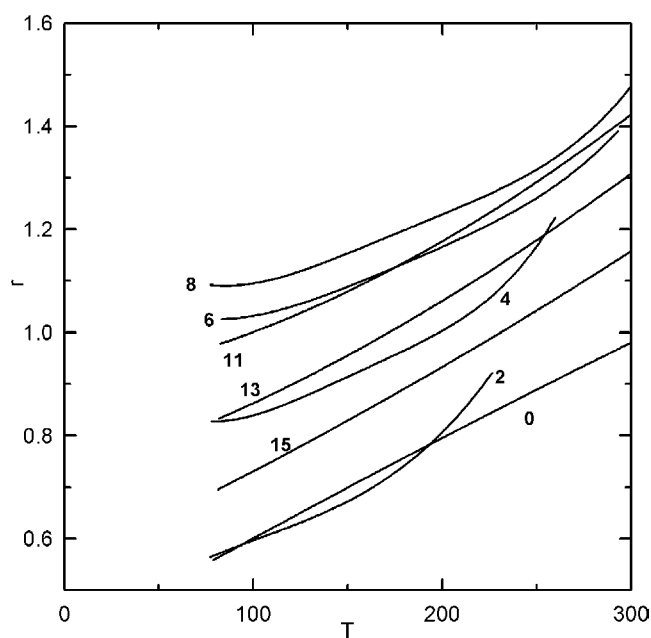


Figure 8. Temperature dependence of the electrical resistance of $\text{Pd}_{0.95}\text{Rh}_{0.05}\text{H}_c$ alloys. $r = R/R_0$, where R and R_0 denote the resistance of the sample in the hydrogenated state at temperature T and in the hydrogen free state at 298 K, respectively. The same meaning of the labels as in figure 5. The upturn deviations at higher temperatures are due to hydrogen desorption.

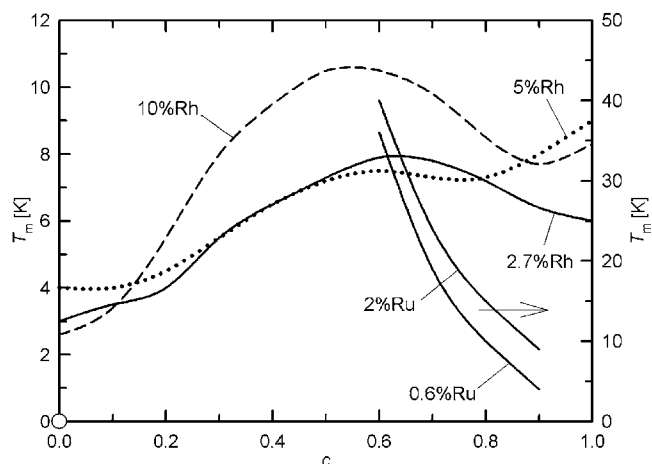


Figure 9. Position of the resistance minimum for Pd/Ru/H and Pd/Rh/H alloys.

All these partial quantities, r_i and a_i , depend on the hydrogen content and alloy composition. The r_{dis} term can usually be identified as the residual resistance, i.e. $r(0)$. It can be measured directly or estimated by an extrapolation of the $r(T)$ relationship from the 80–300 K range. The partial thermopowers, a_i , can be derived from the N–G plots (equation (1)): $a_{ph} = A$, and $a_{dis} = A + B/r_{dis}$.

This procedure fails if the so-called ‘55 K anomaly’ affects the temperature dependence of electrical resistance up to about 150 K. This anomaly is observed in Pd and its dilute alloys with moderate hydrogen contents, $c \sim 0.6$. A deviation from the simple relationships (1) is usually

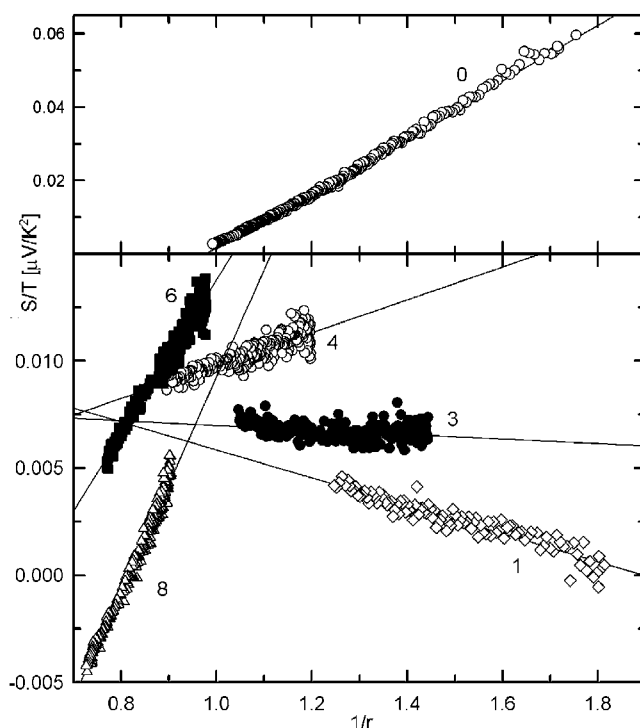


Figure 10. The Nordheim–Gorter plots for $\text{Pd}_{0.95}\text{Rh}_{0.05}$ and $\beta\text{-Pd}_{0.95}\text{Rh}_{0.05}\text{H}_c$ alloys: 1 — $c = 0.98$, 4 — $c = 0.93$, 8 — $c = 0.82$, 0 — $c = 0$.

observed also in the presence of the Kondo-type anomaly. Thus, the partial thermopowers of Pd/Ru/H alloys could only be derived in a few cases.

The derived *disorder* and *phonon* partial thermopowers for H-free and β -phase alloys are shown in figure 11. The *phonon* thermopower for the highly hydrogenated alloys is positive but it decreases with decrease of hydrogen content and finally changes sign. A similar behaviour of the a_{ph} -quantity has been recently observed in hydrogenated Pd alloyed with several early-transition or polyvalent elements [9]. The *disorder* thermopower of the highly hydrogenated alloys is positive (except $\text{Pd}_{0.994}\text{Ru}_{0.006}/\text{H}$ and $\text{Pd}_{0.90}\text{Rh}_{0.10}/\text{H}$) with a tendency for initial increase with decrease of the hydrogen content, within the β -phase region (see also [9]). The behaviour of the a_{dis} -quantity, as referred to the Pd/Rh/H alloys, is more complicated. A comparison of figures 6 and 10 leads to a conclusion that the non-monotonic dependences, TEP versus hydrogen content and TEP versus hydrogen pressure, reflect the non-monotonic dependence of *disorder* thermopower on hydrogen content for the Pd/Rh/H alloy system. The negative value of a_{dis} is the source of negative values of the total thermopower of the $\text{Pd}_{0.98}\text{Ru}_{0.02}$ and $\text{Pd}_{0.90}\text{Rh}_{0.10}$ alloys.

4. Conclusions

The TEP of Pd-based alloys changes qualitatively if transformed into the hydride phase. The strong effect of the solute atoms is preserved in hydrides. The anomalous, non-monotonic, dependence of the total as well as *disorder* partial TEPs on hydrogen content within β -phase regions, as contrasted to $\beta\text{-Pd}/\text{H}$ and other Pd-based hydrides [9], is presumably related to a complex band structure close to the Fermi level. The VBSs of Ru and Rh are

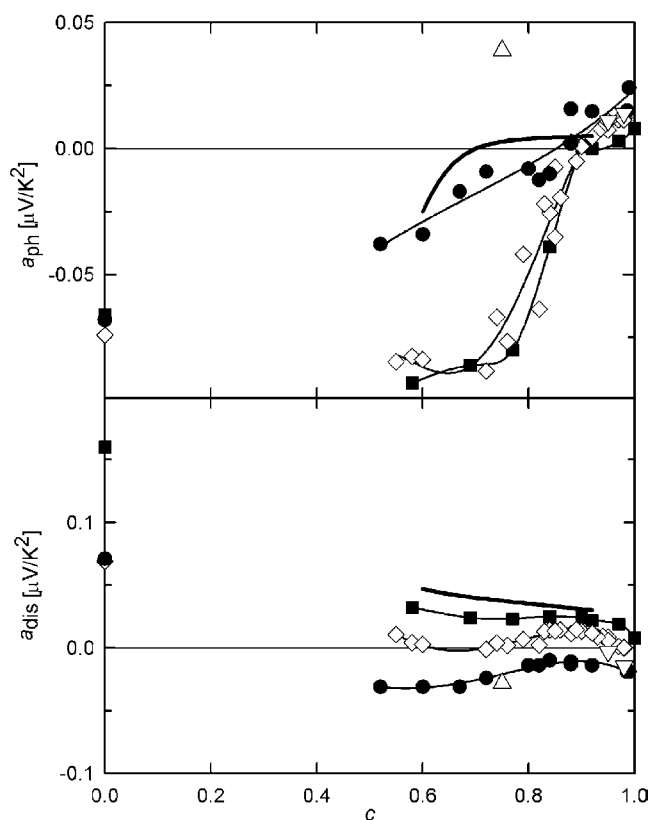


Figure 11. Phonon (a) and disorder (b) partial thermopowers of $\text{Pd}_{1-x}\text{Rh}_x$ and $\beta\text{-Pd}_{1-x}\text{Rh}_x\text{H}_c$ alloys, \blacksquare — $x = 0.027$, \diamond — $x = 0.05$, \bullet — $x = 0.10$, and $\beta\text{-Pd}_{1-x}\text{Ru}_x\text{H}_c$ alloys, ∇ — $x = 0.006$, \triangle — $x = 0.02$. The data for $\beta\text{-Pd/H}$ (thick curves) [8] are shown for comparison.

located, according to the VBS/LMM model mentioned, close to the top of the palladium 4d band. However, because of their finite width, the VBS tails extend to higher energies. When the Fermi level is moving in this energy range, following changes of the hydrogen and solute contents, the influence of the VBS tails on TEP remains important and can also change. On the other hand, as can be seen in figure 9, the VBS tails have minor effects on the electrical resistance.

References

- [1] Switendick A C 1978 *Hydrogen in Metals I* ed G Alefeld and J Voelkl (Berlin: Springer) p 101
- [2] Wicke E and Brodowsky H 1978 *Hydrogen in Metals II* ed G Alefeld and J Voelkl (Berlin: Springer) p 73
- [3] Karolik A S and Golub V M 1998 *Phys. Status Solidi b* **210** 177
- [4] Szafranski A W 1989 *Proc. Int. Conf. on Physics of Transition Metals* vol 2 (Kiev: Naukova Dumka) p 96
- [5] Szafranski A W 1992 *Pol. J. Chem.* **66** 2071
- [6] Wicke E 1980 *J. Less-Common Met.* **74** 185
Wicke E and Fröhlich K 1989 *Z. Phys. Chem., NF* **163** 35
- [7] Szafranski A W 1999 *Phys. Status Solidi a* **175** 665
- [8] Szafranski A W 2002 *J. Alloys Compounds* **340** 54
- [9] Szafranski A W 2001 *J. Alloys Compounds* **316** 82
- [10] Dugdale J S 1977 *The Electrical Properties of Metals and Alloys* (London: Arnold)
- [11] Filipek S M 1989 *Z. Phys. Chem., NF* **163** 627
- [12] Fröhlich K, Severin H G, Hempelmann R and Wicke E 1980 *Z. Phys. Chem., NF* **119** 33
- [13] Huebner R P 1972 *Solid State Phys.* **27** 63
- [14] Blatt F J and Lucke W H 1967 *Phil. Mag.* **15** 649