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CRITICAL MAGNETIC FIELDS OF SUPERCONDUCTING PALLADIUM-HYDRIDES

By M. Horobiowski, T. Skośkiewicz** and E. Trojnar

Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław*

Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw**

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Resistance (R) and magnetization (M) measurements have been carried out on PdH_x ($0.92 \leqslant x \leqslant 0.97$) cylindrical samples in order to determine the critical field $H_c^R(T)$ and $H_c^M(T)$. The form of the magnetization curves suggests that PdH_x is a type I superconductor. The values of $H_c^R(0)$ are significantly higher than $H_c^M(0)$. This is probably due to inhomogeneities in the sample.

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1. *Introduction*

After the discovery of superconductivity in palladium hydride by Skośkiewicz [1] a number of experimental and theoretical papers concerning this problem have been reported. It is well known that pure palladium is a transition metal with strong paramagnetism and no superconductivity. With increasing hydrogen concentration the magnetic susceptibility of the PdH_x system decreases [2] and approaches zero at $x = 0.65$; for higher x the system becomes diamagnetic and superconductivity appears. This gave rise to an explanation that the superconductivity in the PdH_x system results from the quenching of spin fluctuations (paramagnons) [3]. However, it was shown later that, although the quenching of paramagnons favors the occurrence of superconductivity, it alone can not account for the observed T_c in this system. The superconductivity in the PdH_x system occurs primarily because of the existence of optic phonons [4]. The optic modes of PdH_x may make a significant contribution to the electron-phonon coupling. Tunneling experiments seem to confirm this point of view [5].

* Address: Instytut Niskich Temperatur i Badań Strukturalnych PAN, Próchnika 95, 53-529 Wrocław, Poland.

** Address: Instytut Chemii Fizycznej PAN, Kasprzaka 44/52, 01-224 Warszawa, Poland.

The transition temperature T_c into the superconducting state for PdH_x strongly increases with increasing concentration of hydrogen and attains a value of 9 K for $x = 1$ [6].

To prepare PdH_x samples different methods are used: 1) method of electrolytically loading, 2) ion implantation technique, 3) quench condensation onto liquid helium cooled substrates and 4) charging under high hydrogen gas pressure.

The critical field values $H_c(0)$ at $T = 0$ K for $x \approx 1$ obtained by different authors vary from 700 A/cm [7] to 2000 A/cm [8]. Usually, resistance measurements in the applied field give higher values for $H_c(0)$ than diamagnetic moment measurements. Up to now, the shape of the magnetization curves has not given the exact answer to the problem "what type of superconductor is PdH_x?". That is because it is difficult to obtain homogeneous PdH_x samples. In this work some attempts are made to obtain PdH_x samples of high homogeneity.

2. *Experimental procedure*

The samples used in this work were in cylindrical form, 10 mm long and 2 mm in diameter. For hydrogen charging the high pressure technique has been applied [9]. The palladium samples were placed in a high pressure vessel with gaseous hydrogen under a pressure of up to 20 kbar. The samples were kept under high pressure for several days. After saturation of the samples with hydrogen, the high pressure vessel was cooled down to about −50°C and the specimen was removed and placed in a cryostat with liquid nitrogen. For the measurements the samples were mounted under liquid nitrogen and transfered into a helium cryostat in about two-three seconds.

The magnetization measurements were made using a flip coil method. Before each magnetization curve was taken the specimen was heated above T_c in zero field to remove the trapped flux.

To determine the superconducting transition temperature, the magnetic susceptibility of the sample was measured by the a.c. mutual inductance method. The critical temperature was defined as a temperature at which susceptibility reached half of its maximum value. The width of the superconducting transition was dependent on the homogeneity of the sample and did not exceed 0.1 K.

For the electrical resistance measurements an d.c. current of 5 mA was passed through the sample and the voltage drop was measured as a function of the magnetic field or temperature. The resistive transition in the applied magnetic field was spred out in the range at about 70 A/cm. The effect of heating by a current passing through the sample was not observed.

3. *Results and discussion*

We have prepared five samples saturated under various pressures of gaseous hydrogen. The hydrogen concentrations x = H/Pd for these samples were estimated from the measured values of the transition temperature T_c, using $T_c(x)$ graphs published in papers [6, 9].

TABLE I

Sample No	$x = $ H/Pd	$T_c \pm \Delta T$ [K]	Δx	$\varrho \cdot 10^{-6}$ [$\Omega \cdot$ cm]
1	0.920	4.20±0.1	0.0025	2.950
2	0.929	4.72±0.01	0.0003	2.450
3	0.935	5.00±0.08	0.0015	2.009
4	0.947	5.65±0.05	0.001	1.750
5	0.969	6.99±0.02	0.0004	0.785

The values of T_c, the widths (ΔT) of the superconducting transition in zero applied field and the estimated values of hydrogen concentration (x) are listed in Table I.

Fig. 1 shows the magnetization curves obtained at $T = 3$ K for all five investigated samples. The shapes of these curves seem to indicate that the samples are type-I superconductors.

We have defined the critical field H_c^M as a field at which the tangent to the steeply decreasing part of the magnetization curve at the inflection point intersects the abscissa axis (with the high-field tail being neglected). Critical field H_c^M, as a function of temperature, is given in Fig. 2 for all five samples studied in this experiment.

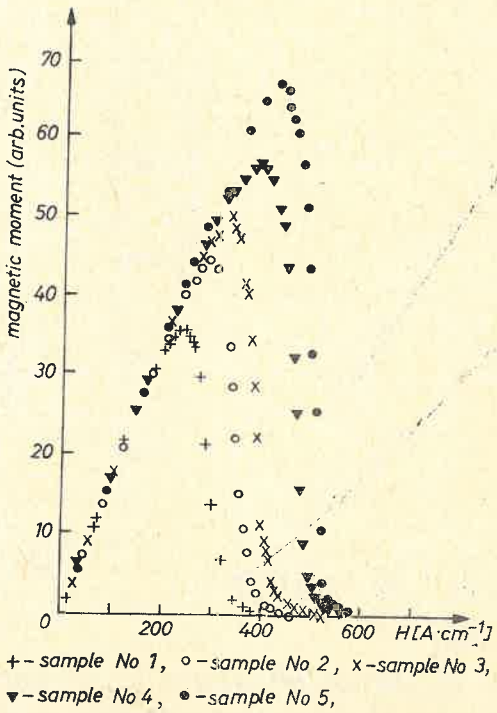

Fig. 1. Magnetization curves for five different samples at constant temperature $T = 3$ K

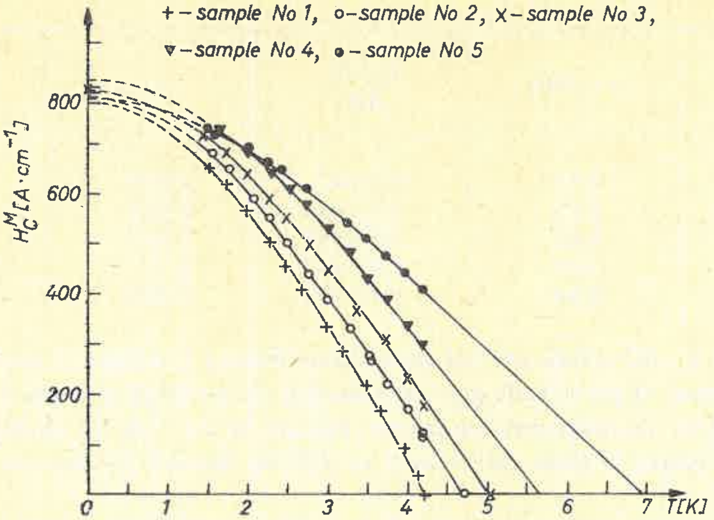

Fig. 2. Critical magnetic field H_c^M of the PdH_x samples versus temperature

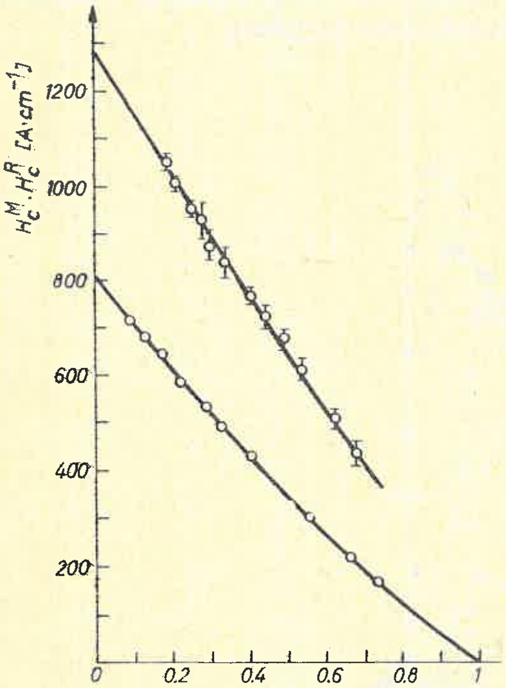

Fig. 3

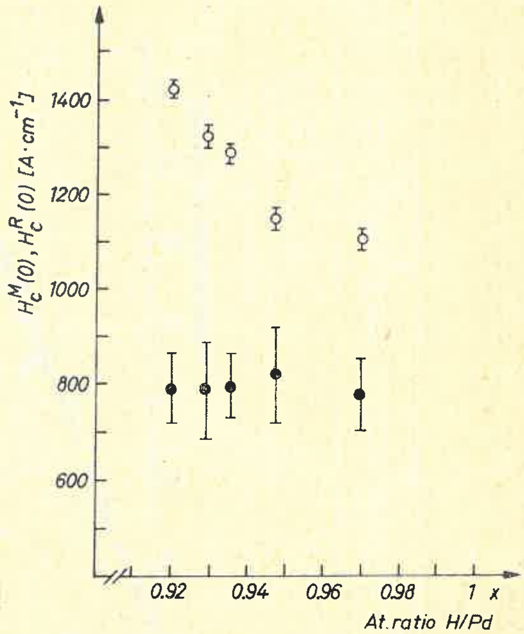

Fig. 4

Fig. 3. Critical magnetic fields H_c^M and H_c^R versus $t^2 = (T/T_c)^2$ for sample No 3

Fig. 4. The extrapolated values of critical magnetic fields $H_c^M(0)$ and $H_c^R(0)$ as a function of hydrogen concentration x

The value of the critical field can also be determined from the resistance measurements as a midpoint of the transition range; it is denoted by H_c^R.

Fig. 3 presents the plot of H_c^M and H_c^R versus $t^2 = (T/T_c)^2$ for one of the samples. Extrapolation of these curves to zero temperature gives $H_c^M(0)$ and $H_c^R(0)$. The values of $H_c^M(0)$ and $H_c^R(0)$ are given in Fig. 4 as functions of hydrogen concentration (x). The values of $H_c^M(0)$ are almost independent of x in the investigated range, $H_c^R(0)$ are much higher than $H_c^M(0)$ for all samples and decrease with increasing hydrogen concentration. It is likely that the high-field tails in magnetization curves extend to $H_c^R(T)$, but the sensitivity of the magnetic moment measurements was inadequate to make such a statement.

Considering H_c^M as the thermodynamic critical field, one may calculate the electron specific heat coefficient using the relation: $\gamma = 0.17\{H_c^M(0)/T_c\}^2$. The values of γ-coefficients obtained in this way are given in Fig. 5 as a function of hydrogen concentration (x). The γ-coefficients decrease with increasing x, as it is found calorimetrically by Zimmermann et al. [10], but the values of γ derived from magnetic measurements in this work are considerably larger. The reason for this is not clear; possibly the values taken as thermodynamic critical fields $H_c^{therm}(0)$ have been too large. The $H_c^{therm}(0)$-values for our PdH_x samples cannot be definitely determined by magnetic moment measurements because of the very high irreversibility. The magnetization curves of these specimens exhibit strong hysteresis (Fig. 6).

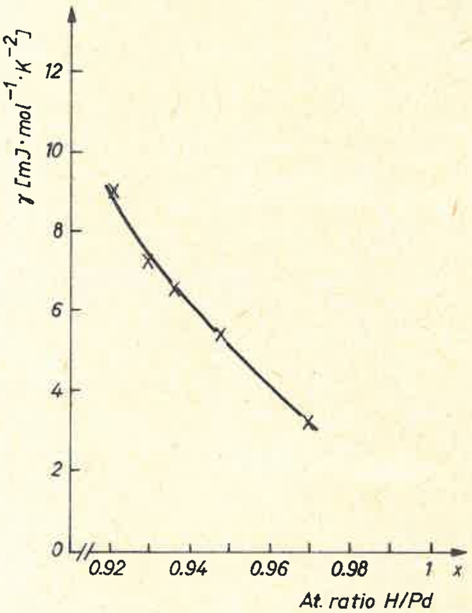

Fig. 5. The values of γ coefficients as a function of hydrogen concentration x

Some authors are of the opinion [8, 11] that PdH_x is a type-II superconductor. However, the magnetization curves derived from our measurements are not typical for such superconductors. As in seen in Fig. 6, the magnetization curves obtainded at T, close to T_c, reminded us of those for a type-II superconductor, but we believe that this form of the curve is caused by inhomogeneities in the sample material [12].

If we treat our samples as type-II superconductors and determine the Ginzburg–Landau parameter κ from the slope of magnetization curves, we can conclude that κ increases

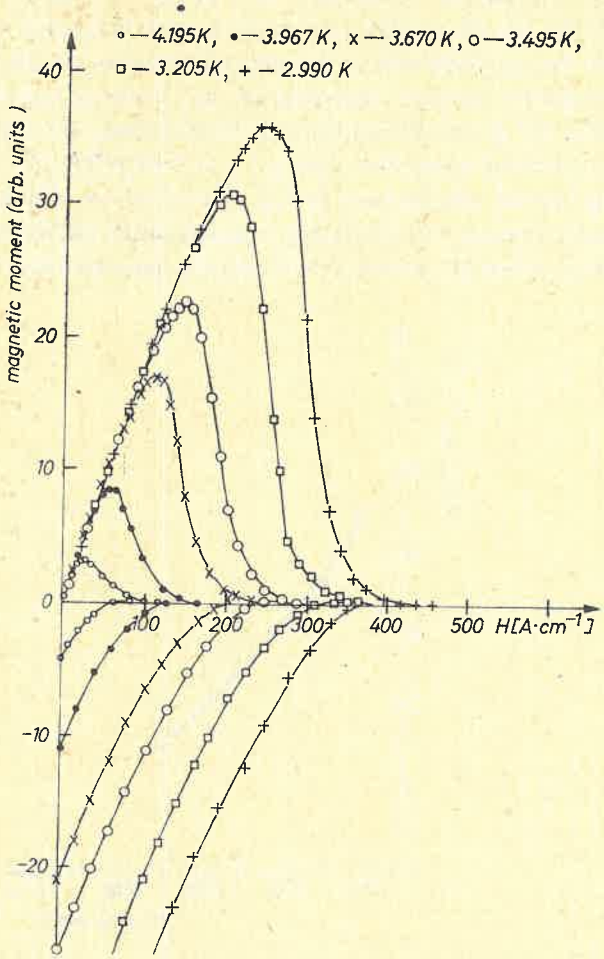

Fig. 6. The magnetization curves of sample No 1 at various temperatures

with increasing temperature which is contrary to the well-known temperature dependence of this parameter.

The role of the inhomogeneities becomes more appreciable near T_c (see Fig. 7). The extrapolation of the $H_c^R(T)$-curve to zero field gives a higher critical temperature than the mutual-inductance and/or magnetic moment measurement. Probably, the inhomogeneities form thin paths with higher critical fields and higher critical temperature than those in the bulk of the sample.

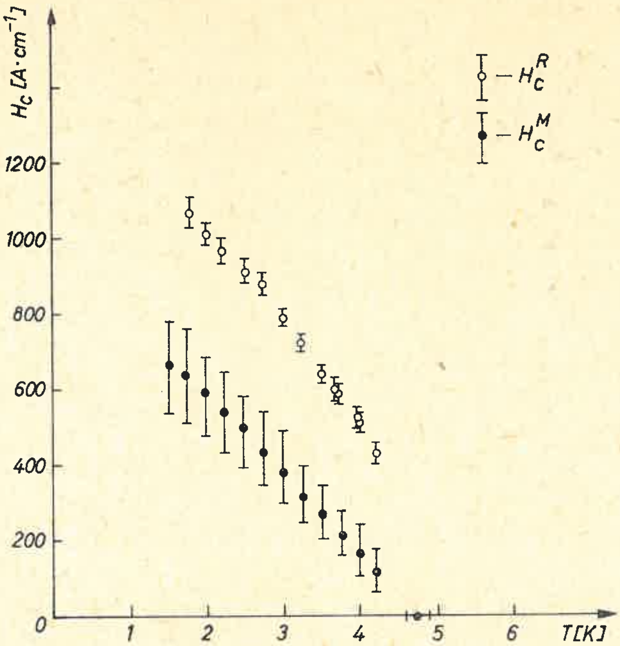

Fig. 7. Critical magnetic fields H_c^M and H_c^R versus T for sample No 2

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