Evidence of Supersoichiometric H/D LENR Active Sites and High Temperature Superconductivity in a Hydrogen-Cycled Pd/PdO

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Introduction I

- Pd metal – no superconductivity (T < 1 mK) due to spin fluctuations; Pd is close to ferromagnetics.
- PdH_x: superconducting at x = H/Pd ≥ 0.8; Tc increases from 1 to 9K when 0.8 < x < 1.0; decrease in spin fluctuations and Sd hybridization.
- Old speculation about metallic hydrogen in PdH_x at x > 1.

Introduction II

- Metallic hydrogen problem: molecular dynamic simulation: at P > 400 GPa hydrogen would be a metallic superfluid with electronic superconductivity (Tc ≥ 100 K) and proton Cooper pairs (E. Babaev, A.Sudbo, N. Ashcroft, PRL, **95**, 105301, 2005).
- Dislocations in H-cycled Pd can absorb large amount of hydrogen (5-6 at. H/1Å of dislocation line)- SANS measurement result.

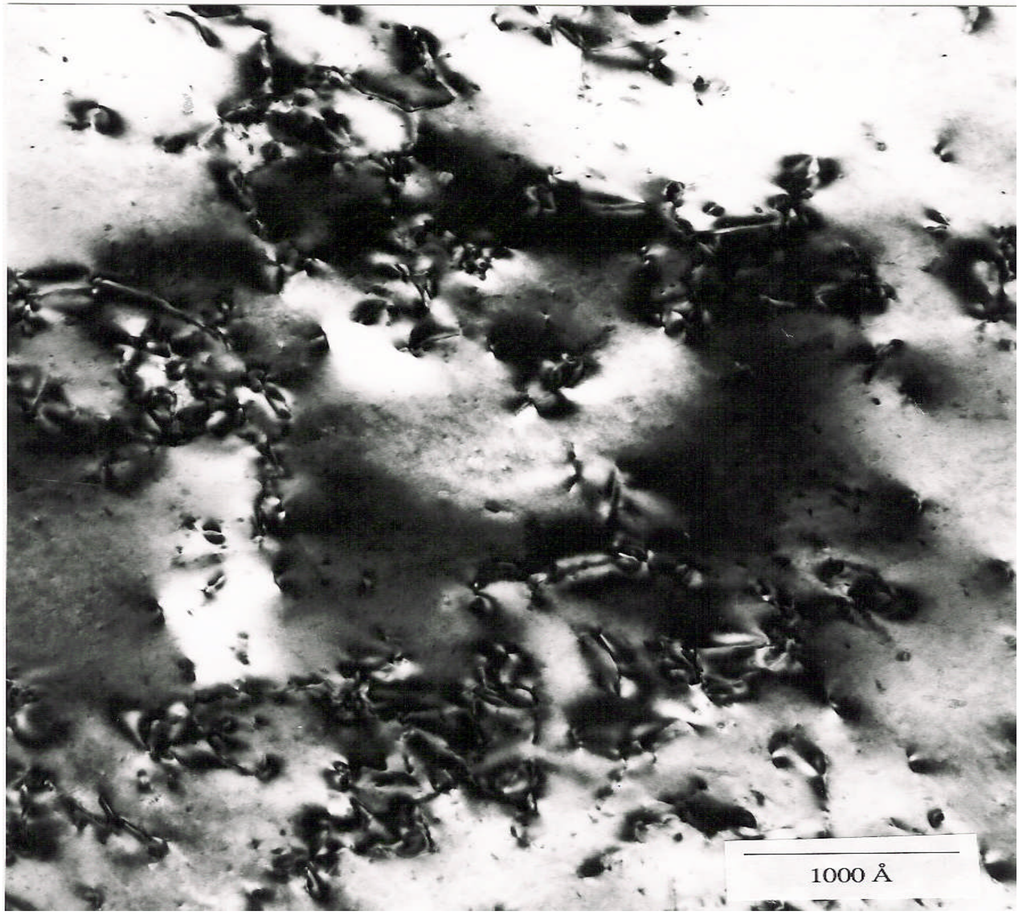
  B.J. Heuser and S.J. King Met. & Material Transaction A29, 1594 (1998).

  Under electrochemical cathode-anodic and/or H2 gas cycling the dislocation density in Pd foils reaches $(2\text{-}5)\times 10^{11}$ cm^{-2}.

  Binding energy of H at deep dislocation cores exceeds 0.7 eV/H-atom

  Hydrogen trapped inside deep dislocation cores may show specific behavior.

Dislocations in the H-cycled Pd single crystal (x 80K)



What is expected ?

If hydrogen trapped inside deep dislocation cores:

- Very high loading ratio x=H/Pd>1 or metallic H_n, $(H_2)_n$ hydrogen phase precipitation
- Enormous compression: P ~ B= 120 GPa,
- High optic phonon frequency ($h\omega \geq 100$ meV).
- Strong electron-phonon coupling ($\lambda_{e-ph} \sim 1.0$).
- Strong Pd-H(D) band overlapping (N. Ashcroft, PRL, 92, 187002, (2004)).
- Excellent Conditions to achieve High Temperature Superconductivity ?

Objectives

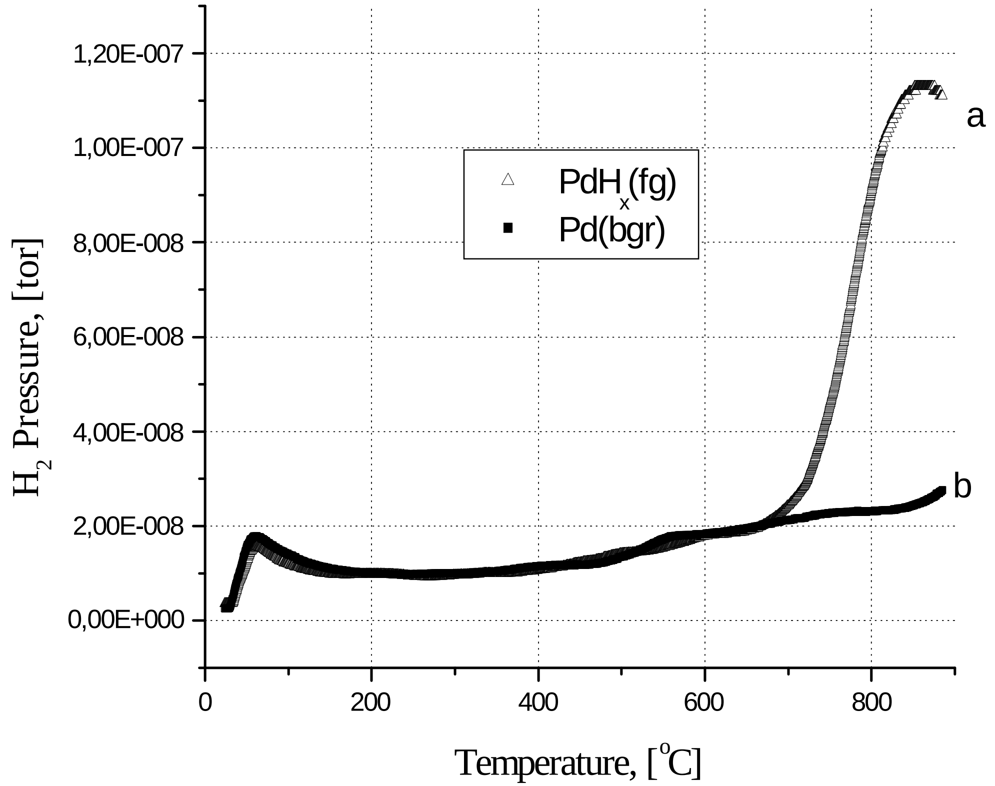
- Study of hydrogen localization inside dislocation cores in Pd and Pd/PdO by vacuum thermal desorption technique.
- Study magnetic and transport properties of condensed hydrogen phase inside dislocation nano-tubes in Pd/PdO foils and Pd single crystal (1.8-300K).
- Define electronic state of condensed hydrogen (metallic ?) within the dislocation network. Search for HTSC in superstoichiometric Pd hydrides.
- Define a role of these superstoihiometric D-sites in LENR to trigger various DD-reactions, including multibody type (3D).

Sample Preparation

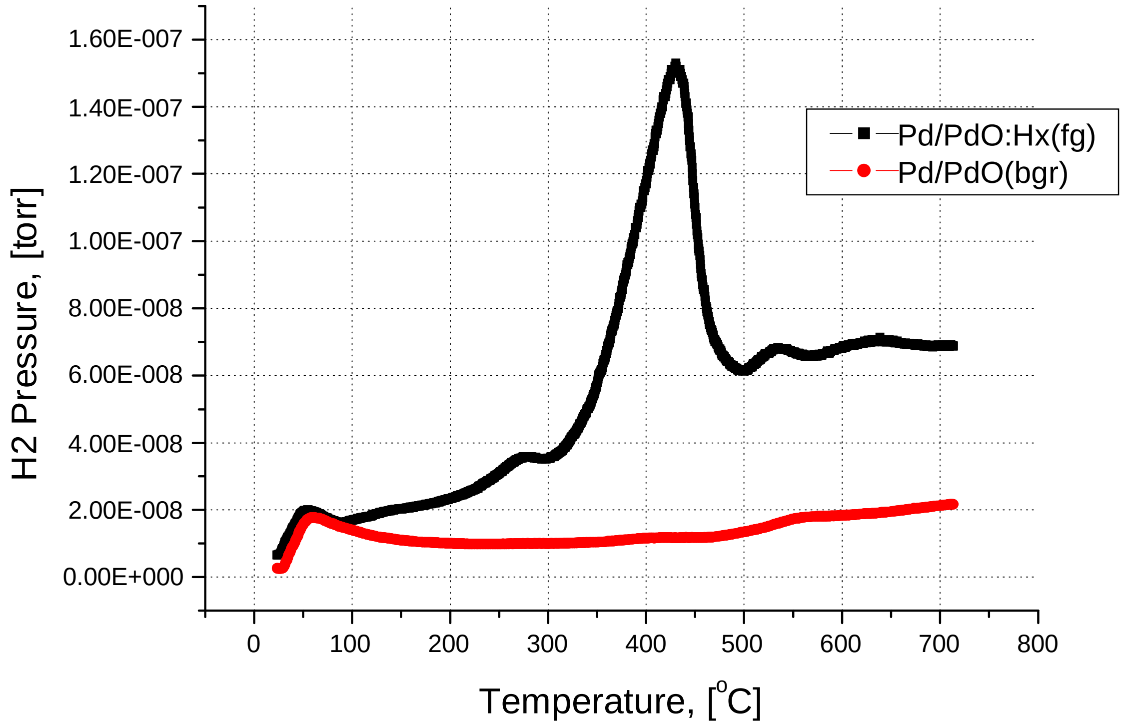
- Pd single crystal ingot (99.999%); samples m=62 mg, H2 gas loading-deloading cycles and annealing at T= 573 K for 2 hr.
- Pd/PdO cold worked heterostructure. h=12.5 μm, (PdO ~ 20 nm), 99.95 %, Nilaco Co., Japan, Fe 10 ppm. Electrochemical cycling (cathode loading-anodic deloading); j=5.0 mA/cm^2, 1MLi_2SO_4/H_2O, annealing at T=573 K.
- Measurements: TDA with mass-spectrometer;
- 1T-SQUID "Quantum Design" MPMS-3, DC and AC modes, M(T), M(H), X'(T), X"(T); sensitivity better than 5x10^{-8} emu/g
- 4 and 2 -probe resistance: R(T), R(I). Keithley182 digital voltmeter; current pulses supplied by Keithley 220 programmable source to exclude thermo-power contribution

Thermal desorption of Hydrogen from Pd:Hx ($x=H/Pd=4.5 \times 10^{-4}$). T_{max}=870 °C, ε_H = 1.6 ±0.2 eV

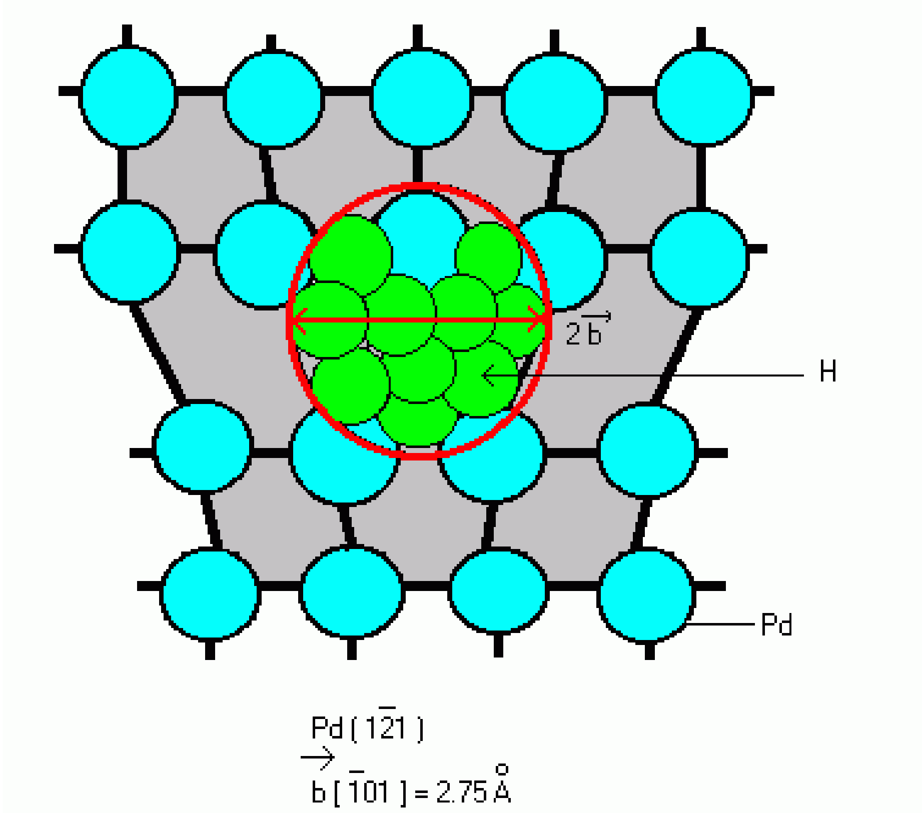
$\varepsilon_H = k_B [T_2 T_1/(T_2 - T_1)] \cdot \ln(P_2/P_1)$ Garlick-Gibson formula for activation energy of hydrogen.



H-Thermal Desorption from $Pd/PdO:H_x$ ($x = H/Pd \sim 6.0 \times 10^{-4}$), $T_m = 440\ °C$, $\varepsilon_H = 0.65 \pm 0.10$ eV



Edge dislocation core in Pd with H_n-"metallic" hydrogen phase: Dislocation core is a nanotube with radius R_H = b (Burgers vector)



Effective Hydrogen Concentration at deep dislocation core ((M. Maxelon et al, Acta Mater. **49/14**, 2625, (2001):

$$\mathbf{x_{eff} = \alpha<[H]/[Pd]>/\pi\rho_d R_H^2},$$

$$(\alpha = a_0/b)$$

a) for PdH_x : $x= <[H]/[Pd]> = 4.5x10^{-4}$

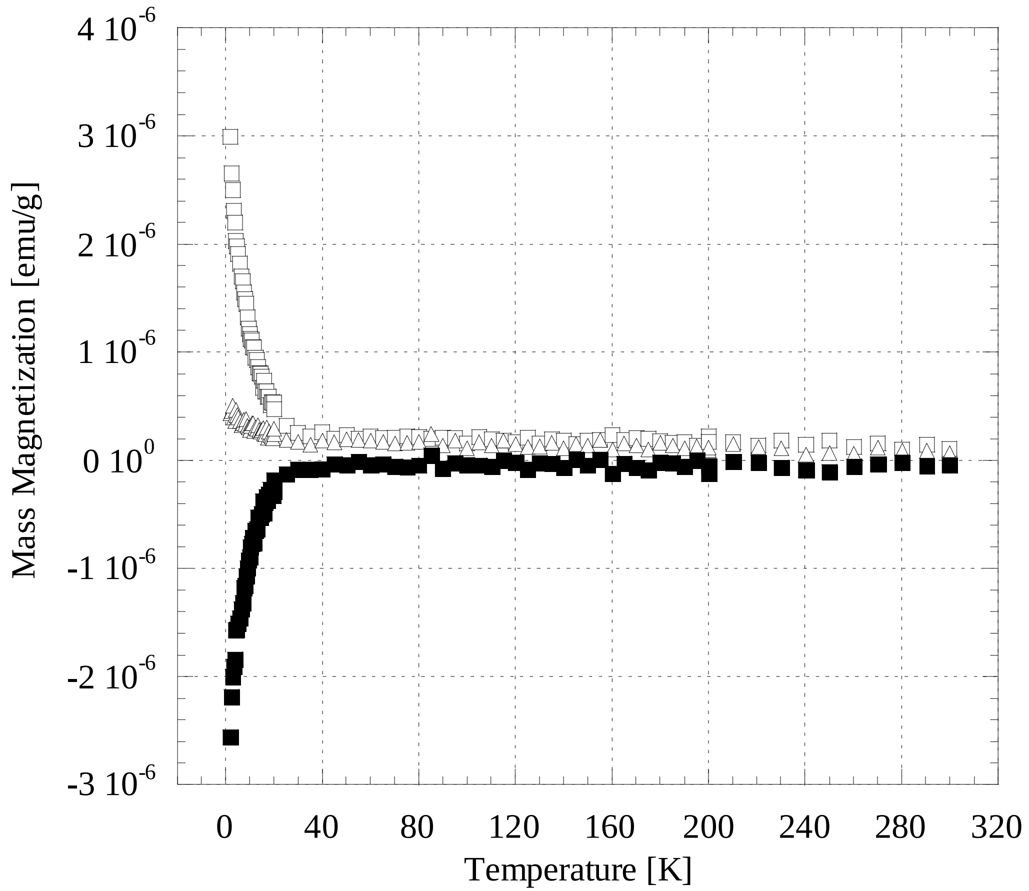
$\rho_d = 2x10^{11}\ cm^{-2}$, $R_H = b = 2.75$ Å

$x_{eff} = 1.35.$

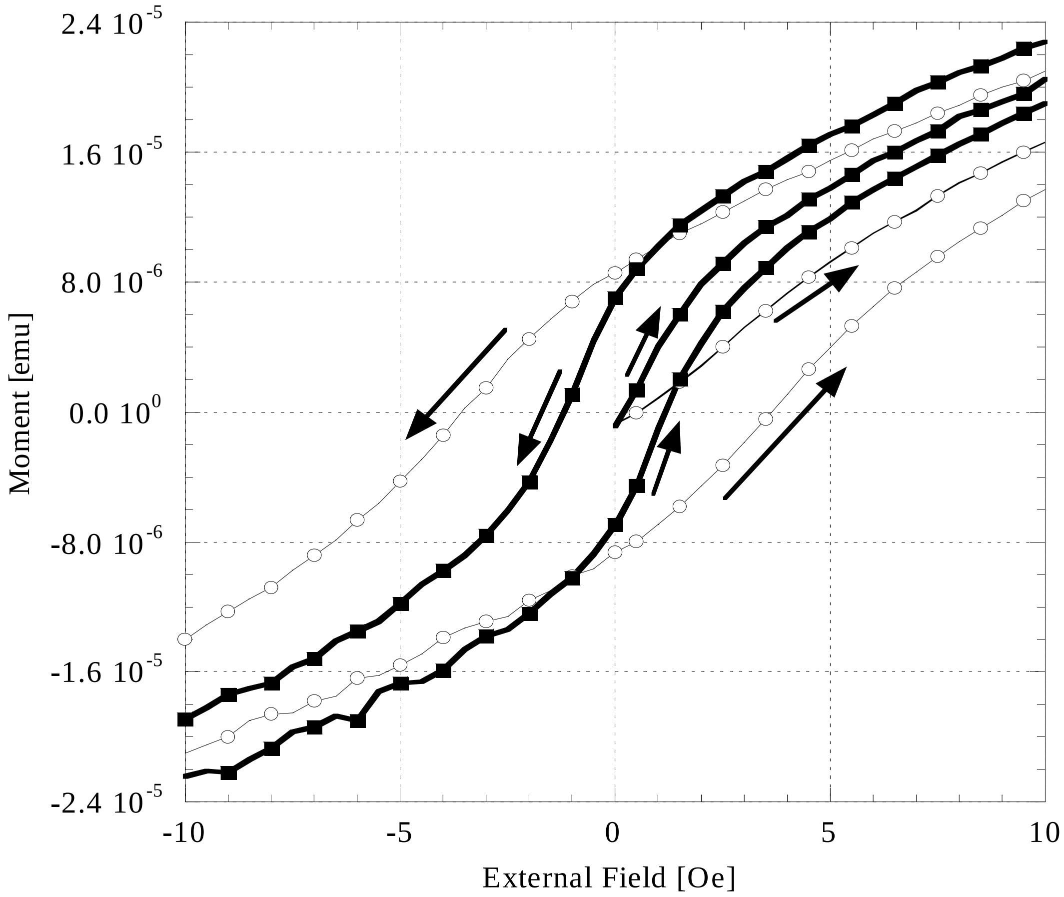
b) for Pd/PdO:Hx: $x= <[H]/[Pd]> = 6.0\ x10^{-4}$,

$x_{eff} = 1.8$

DC Magnetic SQUID measurement with PdHx and Pd single crystal: M(T), H=1.0 Oe

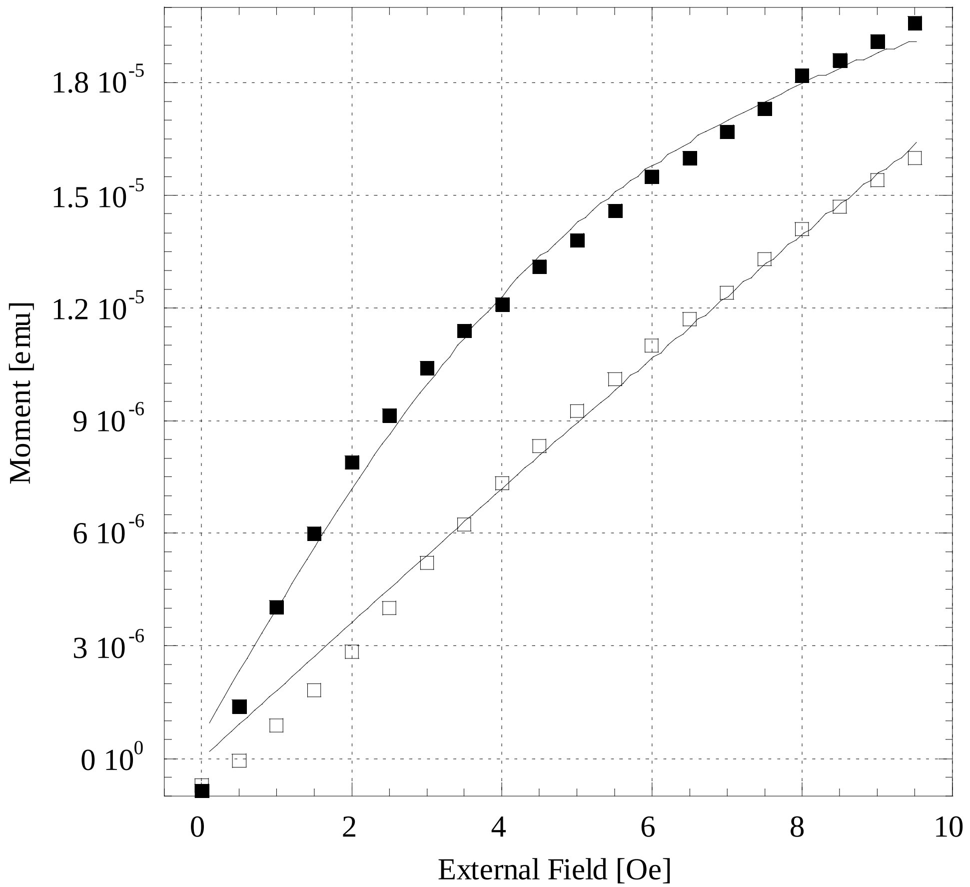


Hysteresis loops for Pd and PdHx single crystal at T=2.0 K

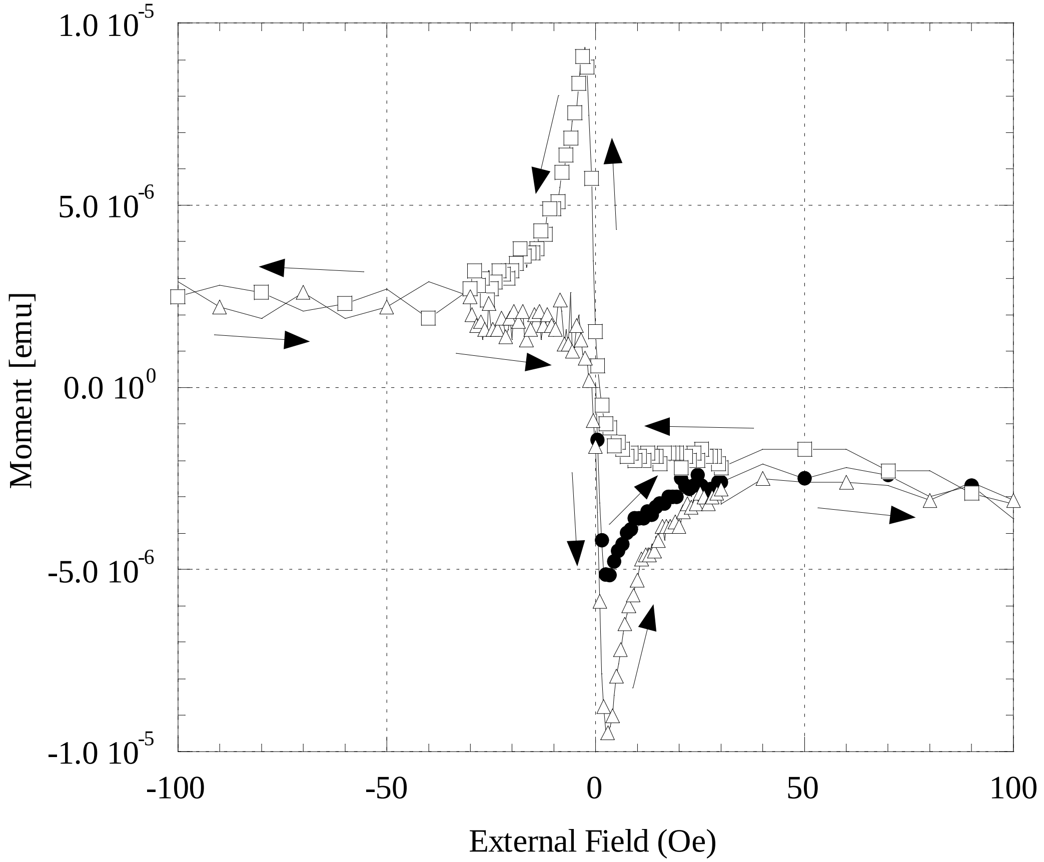


Initial magnetic moment versus external field for annealed Pd (solid boxes) and PdHx (open boxes). Fits to the Langevin function describing the paramagnetic response are shown.

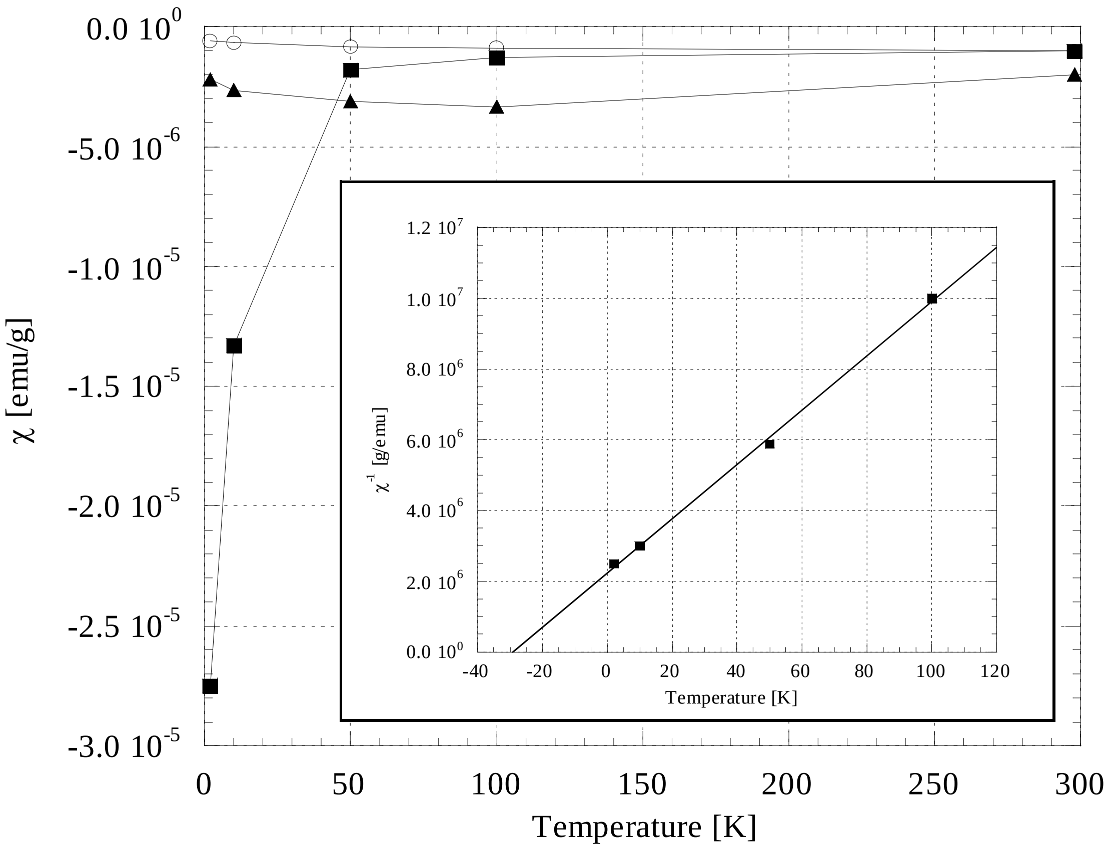
$$M = M_0[\coth(\mu H/k_B T) - (k_B T/\mu H)],$$



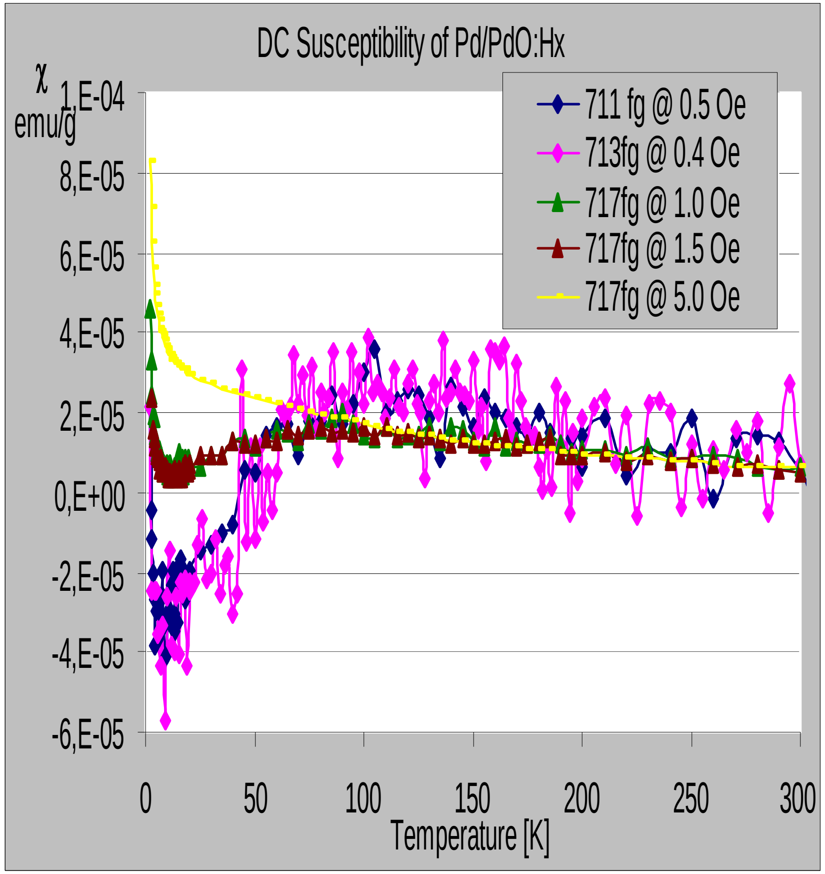
Net magnetic moment (PdHx-Pd) versus external field at 2 K. The strong diamagnetic response at low field (<5Oe) and irreversible behavior are characteristic of a type II superconductor with magnetic flux pinning.



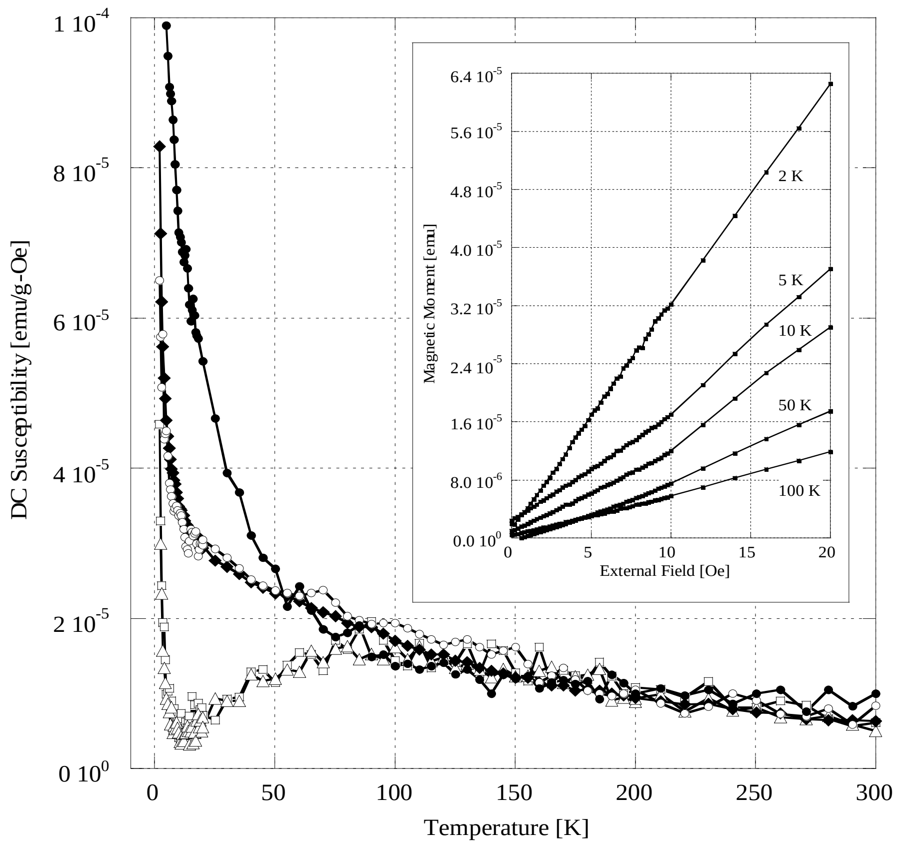
Magnetic susceptibility versus temperature for the net data at high field (open circles), the net data at low field (solid boxes), and 150 nm colloidal Pd (solid triangles). The low-field net susceptibility exhibits a diamagnetic transition below 50 K. Inset: antiferromagnetic Curie –Weiss behavior at H> 10 Oe, Θ = - 29 K



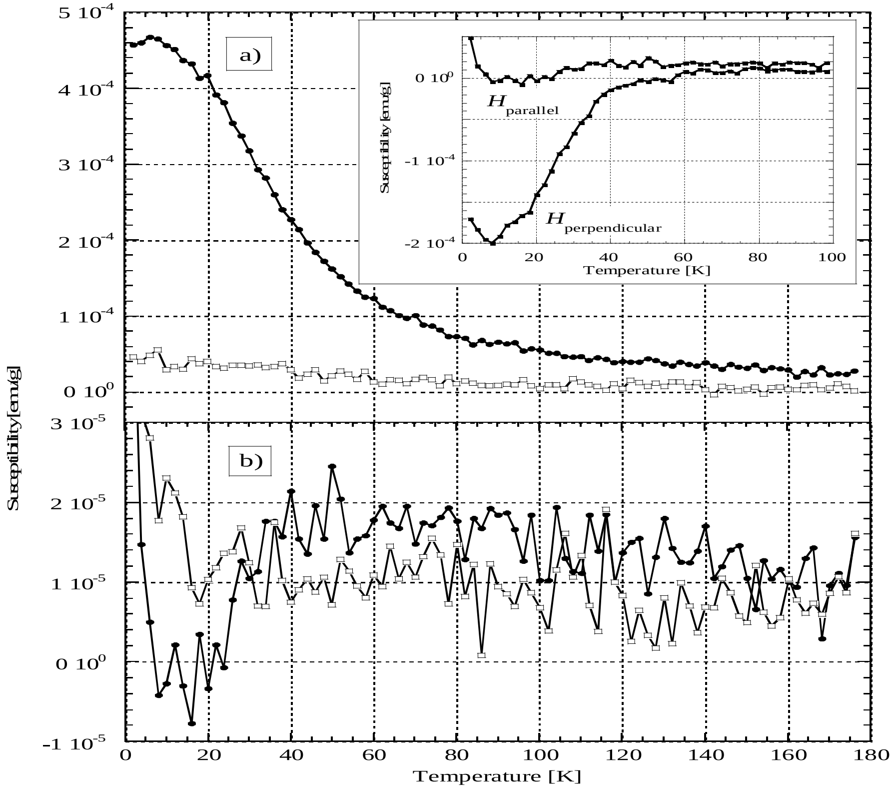
Low magnetic field DC-susceptibility for Pd/PdO:H_x sample: rare DC diamagnetic transitions at H < 0.5 Oe



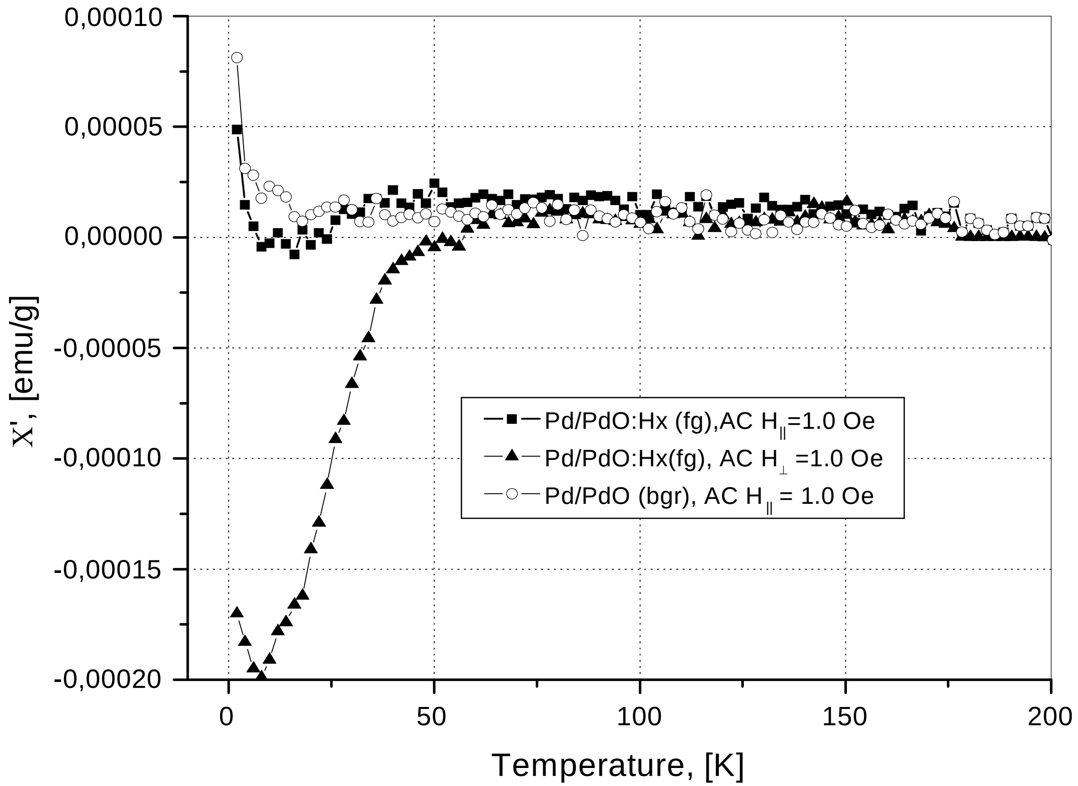
DC susceptibility versus temperature for Pd/PdO:Hx under ZFC at 1.0 Oe (open boxes), 1.5 Oe (open triangles), and 5.0 Oe (solid diamonds), under FC conditions at 1.0 Oe (solid circles), and for Pd/PdO under ZFC at 1.0 Oe (open circles). Inset: low-field magnetization M(H) versus field at T=2-100 K



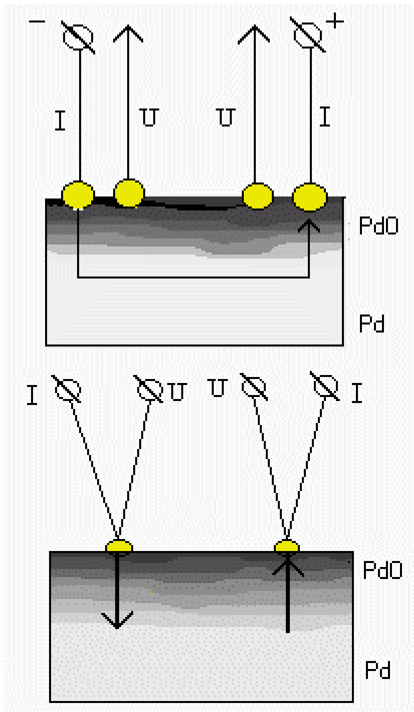
Pd/PdO and Pd/PdO:H_x AC measurement: f = 990 Hz, h=1.0 Oe, H=0



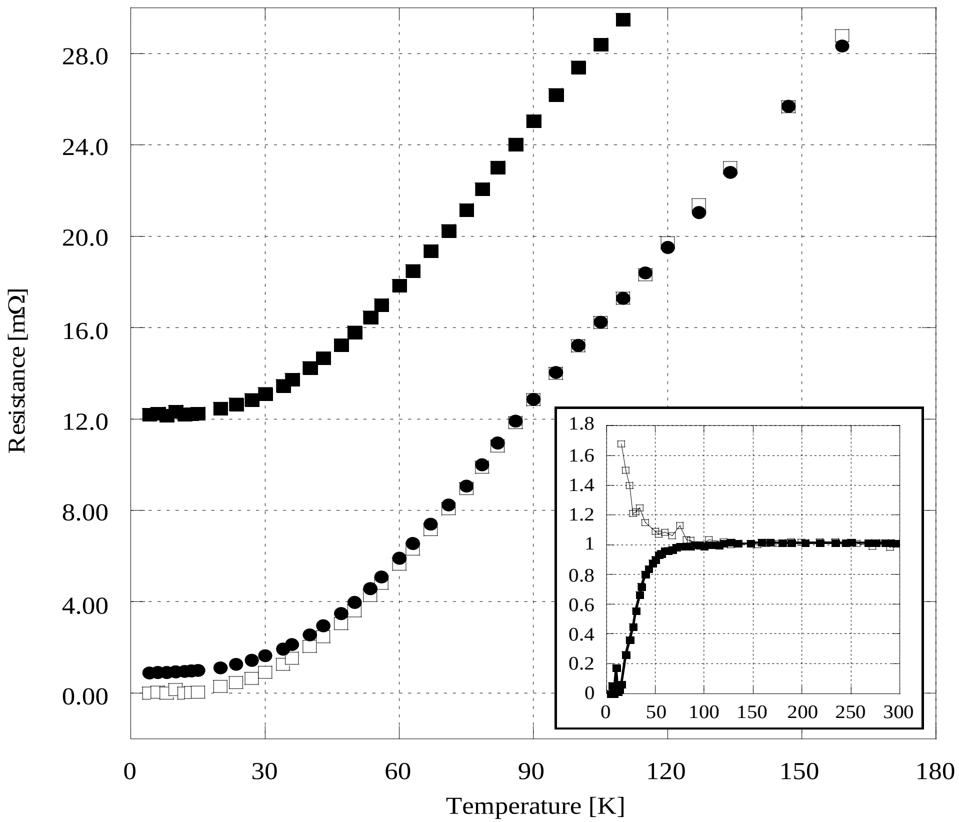
X' AC susceptibility of Pd/PdO:Hx and Pd/PdO-blank samples vs. T for $H_\perp$ and $H_\parallel$ with respect to the sample: $H_\perp / H_\parallel = \xi^2/d^2 = 25$ at T=10 K; d ~ 50 nm (Pd-PdO interface width), ξ ~ 250 nm – 2 dimensional type II Superconductivity



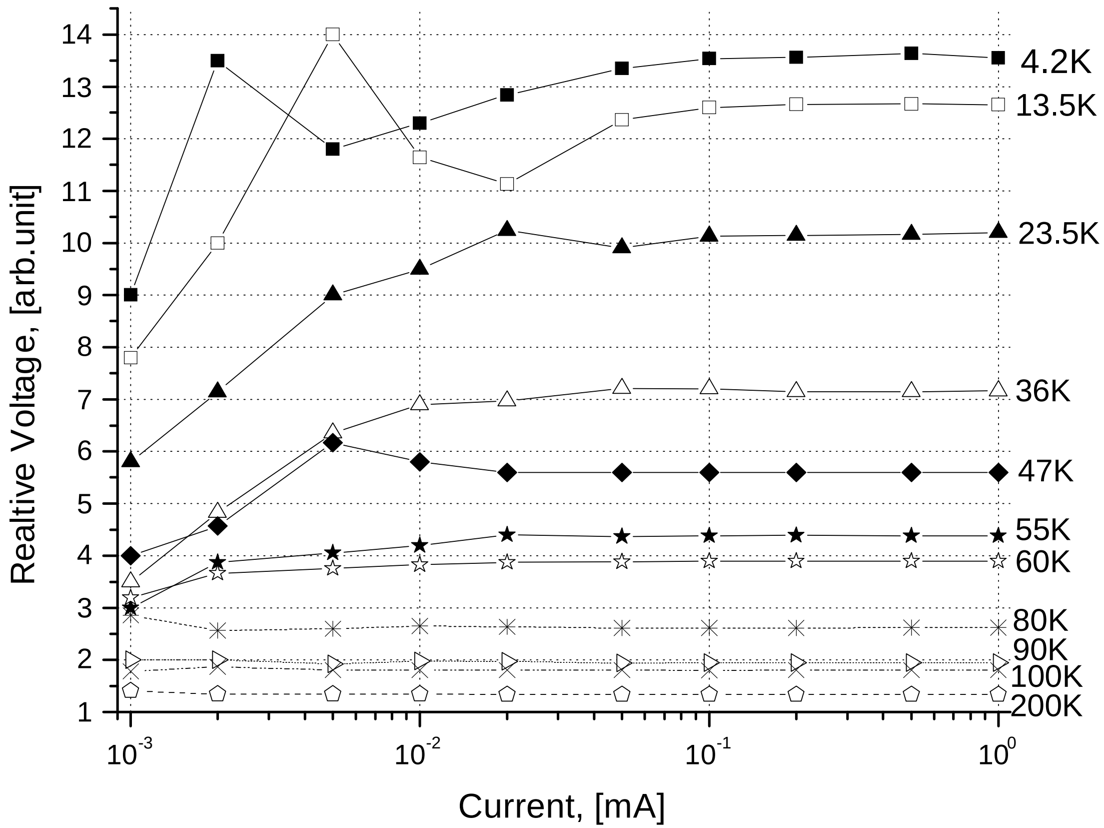
Diagrams of 4-probe and 2-probe(pseudo-four probe) resistance measurements



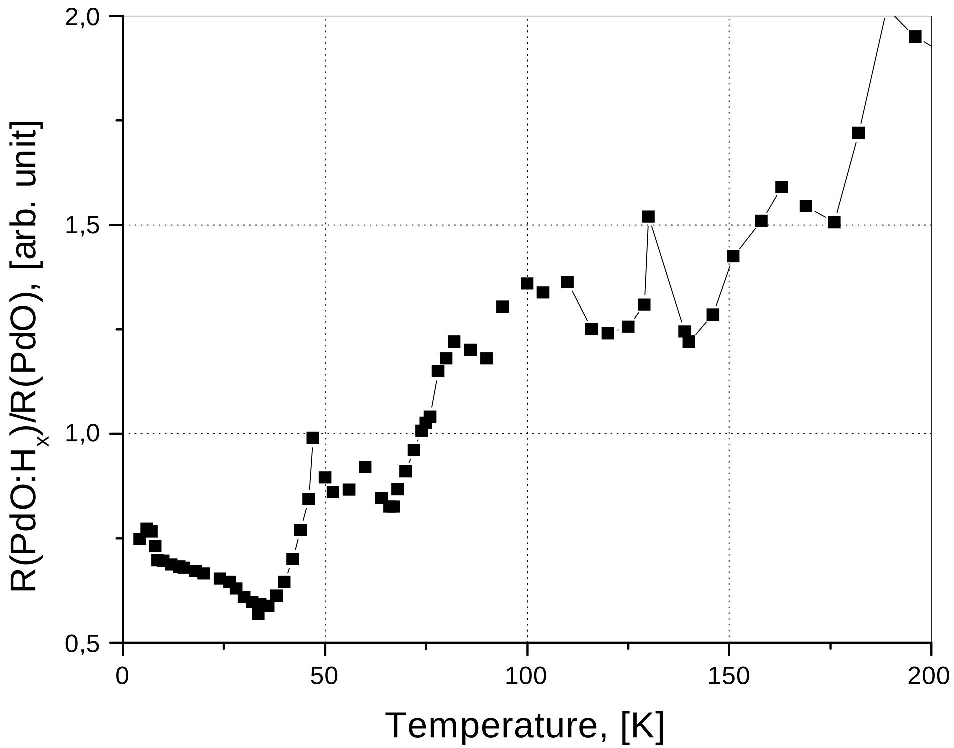
R(T) for Pd/PdO:Hx and blank Pd/PdO. Inset: - Relative resistance (solid boxes)R = R(Pd/PdO:H_x-Ri)/R(Pd/PdO) and temperature coefficient of resistivity (open circles) K=K(Pd/PdOH_x)/K(Pd/PdO)



Normalized V-I characteristics for (Pd/PdOHx)/(Pd/PdO) ratio vs.T. Resistance decrease with decrease in I below 60 K.



2-probe resistance measurement: Relative resistance of Pd-PdO:H_x boundary [R(Pd/PdO:H_x)/R(Pd/PdO)] vs. T. R(Pd/PdO:H_x) < R(Pd/PdO) at T < 75 K



Signatures of Filamentary Superconductivity in $Pd/PdO:H_x$

- The non-linear behavior at low current (<0.01 mA) and low temperature (≤50 K) indicate enhanced transport properties consistent with uncorrelated supercurrents that break down at high current and high temperature (T > 67 K).
- In the present case, the non-linear behavior associated with the suppression of weak superconductivity along a network of condensed hydrogen at dislocation cores analogous to a Josephson medium. Similar filamentary superconductivity has been previously observed in high-Tc superconductors

McMillan's estimate for T_c

$T_c = \{<\hbar\omega>/1.2k_B\}\times \exp\{1.04(1+\lambda)/[\lambda-\mu^*(1+0.62\lambda)]\}$ – McMillan equation for T_c vs. characteristic average phonon energy $<\hbar\omega>$, e-p coupling constant λ and Coulomb pseudodopotential μ^*

a) PdH_x: $\mu^* = 0.1$, $<\hbar\omega> \sim$ 58-105 meV, $x_{eff} = 1.35$, $\lambda = 0.643$: $T_c \sim$ 18-40 K:

b) Pd/PdO:H_x: $\mu^* = 0.1$, $<\hbar\omega> \sim$ 58-105 meV, $x_{eff} = 1.8$, $\lambda = 0.892$: $T_c \sim$ 40-70 K

Summary of results

- $Pd:H_x$ and Pd/PdO:Hx samples after H-cycling and annealing at T=573 K contain only condensed hydrogen phase inside deep dislocation cores: x=H/Pd = (4-6) x 10^{-4} with respect to the sample. Inside dislocation nanotube x=H/Pd ~ 1.4-1.8.
- Accordingly to SQUID measurements the H2-cycled PdHx single crystal sample demonstrates signature of a weak type II superconductivity, involving condensed hydrogen phase in deep dislocation cores [PdH_x-Pd] below 30 K.
- Results of both magnetic and transport measurements in Pd/PdO:Hx are suggested superconducting transition below 70 K. Reproducible Meissner-effect was obtained at $H \leq 1.0$ Oe in AC field (f = 1 kHz): Type II 2-dimensional filamentary SC.

Conclusions

- Deep dislocation cores in Pd could be considered as a H-dominant Pd hydride (x =H/Pd > 1.0) sites showing HTSC properties.
- **On the way**: Pd nanowires and Pd/PdO multilayer structures to increase SC volume fraction with respect to Pd matrix.

Publications:

- A.G. Lipson, B.J. Heuser, C.H. Castano and A. Celic, "Observation of a low –field diamagnetic contribution to the magnetic susceptibility of deformed single crystals PdHx", Phys. Lett. A **339**, 414-423 (2005).
- A.G. Lipson, B.J. Heuser, C. H. Castano, G.H. Miley, B.F. Lyakhov and A.V. Mitin, "Transport and Magnetic Anomalies in a Hydrogen-Cycled Pd Foil with a Thermally-Grown Oxide Below 70 K", Phys. Rev. B **72**, 082541 (2005).

Conclusions and LENR connection

- Deep dislocation cores in Pd/PdO could be considered as a H/D-dominant Pd hydride (x =H/Pd ~ 2.0) sites suggesting HTS properties.
- Triggering of LENR at such sites should be easier than in regular lattice due to:
- - shortest DD-distance (close to Bohr radius)
- - highest D-loading and lattice compression
- - effective electron screening
- - large optic phonon energy ($\hbar\omega_D \geq 100$ meV) resulting in a most effective lattice-nuclei energy transfer.
- Metallic H/D superfluid suggests dramatic enhancement of quantum entanglement between deuterons at those sites

Acknowledgments

- This work was partially supported by the NSF under Grant No. DMR-9982520 and by New York Community Trust. The magnetic measurements were performed at the Frederick Seitz Material Research Laboratory at UIUC supported by the U.S. Department of Energy under Grant No. DEFG02-91-ER45439.
- Special thanks to Prof. A. Bezryadin (UIUC) and Prof. R. Prozorov (Univ. South Carolina) for useful comments.