THERMOELECTRIC POWER OF CONCENTRATED PdH

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THERMOELECTRIC POWER OF CONCENTRATED PdH

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Résumé.- Le pouvoir thermoélectrique (PTE) de PdH a été mesuré entre 10 et 170 K pour les concentrations comprises entre 0,915 et 0,996. Tous les échantillons présentent un PTE sans aucune trace de maximum caractéristique du "phonon-drag". La valeur du PTE diminue lorsque la concentration augmente ; ceci est attribué à l'accroissement correspondant de la branche optique du spectre de phonons.

Abstract.- The thermoelectric power of PdH was measured between 10 and 170 K for H concentrations between 0.915 and 0.996. All samples showed a positive thermopower with no hint of a phonon drag peak. The decrease with concentration is attributed to the rise of the optical phonon branch.

The thermoelectric power of pure Pd is negative at room temperature, indicating a decreasing density of states at E_F. For x = H/Pd $\sim$ 0.7, the thermopower increases monotonically as a function of temperature between 30 and 110 K /1/. When x → 1 we expect a pseudo-silver behaviour, with a positive thermopower, in the same way that NiH behaves like pseudo-copper /2/.

We have measured the thermopower of very concentrated PdH between 10 and 170 K. x varied from 0.915 to 0.996. The hydrides were prepared electrolytically at -78°C, using the method described in /3/. The hydrogen content was determined from the resistivity, using the data of /3/ and /4/. The thermopower was measured by establishing a temperature gradient across a Pd - PdH thermocouple. A Au + 0.06 % Fe versus chromel thermocouple measured the temperature difference. The bottom end of both thermocouples was held at a fixed temperature, which was a liquid helium bath (4 K) for measurements in the range 10-80 K and a liquid nitrogen bath (77 K) for the range 80-170 K. The thermal voltage was fitted to a fourth-order polynomial, which was differentiated to obtain the Pb-PdH thermopower. The absolute value of the PdH thermopower was then obtained by subtracting the published values for Pb /5/. Overall accuracy is estimated at ± 0.2 μV/K. The results are shown in figure 1.

The most noticeable feature is the total absence of a phonon-drag hump, which is still visible for x $\sim$ 0.7 at about 20 K /1/. It may be present, although very small, below 10 K, since Fletcher et al. found a small effect at 8 K for x = 0..77 /6/.
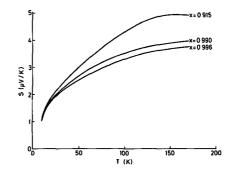

Fig. 1 : The observed thermoelectric power of PdH$_x$.

The thermopower at 170 K varied between 3 and 5 μV/K, which is much higher than that for silver ($\sim$ 1 μV/K). In NiH the value is estimated to be $\sim$ 1.3 μV/K /7/, which is very close to copper. It is interesting to speculate why these two hydrides should behave so differently. It may be noted that PdH has a low-lying optical phonon band /4/, while NiH has not /8/. PdH is a superconductor, while NiH is probably not /8/. This is most probably due to the much higher value of the Einstein temperature for NiH ($\sim$ 1200 K /8/ against $\sim$ 600 K for PdH /4/). The matter bears further investigation.

At temperatures above 100 K the thermopower of PdH is positive and increases with H concentration in the range 0.1 < x < 0.7 /1/. It is thus of interest to note that in the range 0.9 < x < 1 the thermopower decreases with H concentration. This is attributed to the rise of the optical phonon resistivity.

The theoretical electron diffusion thermopower of a metal can be written as /9/

$$S_{th} = S_o \left[\partial \ln \sigma(E)/\partial \ln E\right]_{E_F} \qquad (\alpha)$$

where $S_o = \pi^2 k^2 T/3e \, E_F$

$\qquad = 12.45 \times 10^{-8} \, T/E_F \quad V/K$

where E_F is in eV. Taking $T = 170$ K and $E_F = 5.5$ eV
(the free electron value corresponding to silver),
we have $S_o = -0.76 \, \mu V/K$. The free electron model
has been used to derive this. However, from super-
conducting critical field measurements /10/ it ap-
pears that the specific heat constant γ is rougly
double that of the free electron value. This could
double S_o to $-1.5 \, \mu V/K$. Hence $\left[\partial \ln \sigma(E)/\partial \ln E\right]_{E_F}$
~ -3. Now

$$\ln \sigma(E) = \ln \tau(E) + \ln v(E) + \ln A(E)$$

where τ is the relaxation time, v the Fermi veloci-
ty and A the area of the Fermi surface. If the lat-
ter touches the zone boundary, we expect A(E) to be
a slowly decreasing function of E, as in the case
of silver. It is more difficult to see how τ de-
creases sufficiently fast with energy to give the
required value of -3.

The observed thermopower is given by the
Nordheim-Gorter rule as

$$S = \Sigma \, S_i \, \rho_i / \Sigma \rho_i$$

where S_i is the theoretical contribution from pro-
cess, which yields resistivity ρ_i. Since the obser-
ved thermopower decreases as x increases (and the
optical resistivity increases /11/) we assume that
there is no contribution to S from the optical band
i.e. $S_{op} \simeq 0$, so that

$$S = S_{ac}\left[\rho_{ac}/(\rho_{ac} + \rho_{op})\right] \qquad (\beta)$$

where S_{ac} is given by (α) above. The ρ's plotted by
Chiu and Devine /11/ at $T = 210$ K are tabulated
below :

x	$\rho_{ac}(\mu V \cdot cm)$	$\rho_{op}(\mu V \cdot cm)$	$\rho_{ac}/(\rho_{ac}+\rho_{op})$
0.8	1.7	1.0	0.63
0.9	1.9	2.0	0.49
1.0	2.0	3.0	0.40

Assuming linear interpolation, we obtain the follo-
wing fable for our results :

x	$\rho_{ac}/(\rho_{ac}+\rho_{op})$	S(170 K)($\mu V/K$)
0.915	0.47	4.9
0.990	0.41	4.0
0.996	0.40	3.7

The last two columns are roughly proportional,
showing that our simple model is able to explain
the decrease.

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