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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 $x = \text{H/Pd} \sim 0.7$, the thermopower increases monotonically as a function of temperature between 30 and 110 K /1/. When $x \rightarrow 1$ 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 $\pm 0.2 \mu\text{V/K}$. 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 $5 \mu\text{V/K}$, which is much higher than that for silver ($\sim 1 \mu\text{V/K}$). In NiH the value is estimated to be $\sim 1.3 \mu\text{V/K}$ /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 ($\sim 1200 \text{ K}$ /8/ against $\sim 600 \text{ K}$ 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/

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

$$\text{where } S_o = \pi^2 k^2 T / 3e E_F \\ = 12.45 \times 10^{-8} T / E_F \text{ V/K}$$

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 $S_o = -0.76$ μ V/K. The free electron model has been used to derive this. However, from superconducting critical field measurements /10/ it appears that the specific heat constant γ is roughly double that of the free electron value. This could double S_o to -1.5 μ V/K. Hence $\left[\frac{\partial \ln \sigma(E)}{\partial \ln E} \right]_{E_F} \sim -3$. Now

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

where τ is the relaxation time, v the Fermi velocity and A the area of the Fermi surface. If the latter 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 decreases sufficiently fast with energy to give the required value of -3 .

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

$$S = \sum S_i \rho_i / \sum \rho_i$$

where S_i is the theoretical contribution from process, which yields resistivity ρ_i . Since the observed 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. $S_{op} \approx 0$, so that

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

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	ρ_{ac} (μ V.cm)	ρ_{op} (μ V.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 following table for our results :

x	$\rho_{ac}/(\rho_{ac} + \rho_{op})$	$S(170 \text{ K})$ (μ 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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