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Normal state resistivity and superconductivity in $\text{Pd}_{1-y}\text{Ni}_y\text{D}_x$ alloys

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Résumé. — Nous mesurons la contribution des phonons optiques à la résistivité électrique d'alliages $\text{Pd}_{1-y}\text{Ni}_y\text{D}_x$. Cette contribution diminue avec la concentration en nickel en même temps que la température de transition supraconductrice T_c . Une analyse quantitative montre que la décroissance de T_c ne peut être entièrement expliquée par la diminution de la contribution des phonons optiques en couplage electron-phonon. D'autres possibilités sont discutées.

Abstract. — The contribution of optical phonon scattering to the electrical resistivity of $\text{Pd}_{1-y}\text{Ni}_y\text{D}_x$ alloys is determined. This contribution decreases with increasing Ni concentration and is accompanied by a depression of the superconducting transition temperature T_c . A quantitative analysis of our data indicates that the depression of T_c cannot be entirely accounted for by variation of the contribution of the optical phonons to the electron-phonon coupling. Other possible mechanisms are discussed.

1. **Introduction.** — The discovery of superconductivity in PdH_x systems [1, 2] raised the question of the origin of the superconducting state in a material with a low electronic density of states. The positive isotope effect observed for the transition temperature T_c [2], tunnelling experiments [3, 4] and normal state resistivity measurements [5, 6] demonstrated the importance of the coupling between conduction electrons and optical phonons or H vibrations. Furthermore, resistivity data indicate that the optical phonon contribution to the electron-phonon coupling parameter is 2 to 4 times larger than that arising from acoustical phonons. This result, which is supported by theoretical considerations [7], indicates that the main factors governing T_c are the density of electron states at the H site and the value of the optical phonon energy, which is much lower in PdH_x than in most other hydrides.

The first attempts to see how T_c is changed by substitution of Pd with other elements were made by Stritzker [8]. They indicated a substantial increase of T_c for the monovalent elements Cu, Ag and Au. One possible explanation is an increase in the H site density of states. Amongst the elements which can substitute Pd are the isoelectronic elements, Ni and

Pt [9]. Whilst no change in T_c is observed for low Pt concentration, T_c decreases strongly for Ni and extrapolates to zero for about 14 % of Ni. This decrease of T_c should be compared with that observed for magnetic impurities, such as Fe or Cr for which T_c extrapolates to zero for concentrations below 0.1 % [10].

These data raise the question, what causes the drop, in T_c with increased Ni concentration. Is it due to a decrease of the optical phonon contribution to λ which in turn can be related either to electronic effects (a decrease in the H site density of states) or to a hardening of the optical phonons ? Are their magnetic effects caused by the high concentration of Ni despite the fact that it is a non magnetic impurity in most of the simple host metals ?

To answer these questions we present some data on $\text{Pd}_{1-y}\text{Ni}_y\text{D}_x$ alloys where we measure simultaneously the value of T_c and the optical phonon contribution to the electrical resistivity and so to λ . The resistivity technique, contrary to tunnelling density of states measurements, can be applied to non superconducting materials, and, indeed, is used here for the sample of highest Ni concentration, which is non superconducting.

2. **Experiment.** — The Pd-Ni films are prepared on a glass substrate by co-evaporation of Pd and Ni using two electron guns in high vacuum (10^{-8} torr).

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A nominal composition, y , is obtained by monitoring the evaporation rates of both elements using a quartz monitor. We have made two measurements to check this composition. First, we determine the ferromagnetic transition temperature T_{cm} from the variation with temperature of the extraordinary Hall coefficient. This gives us an estimate of y independent of the quartz monitor through the well-established $T_{cm}(y)$ relation [11-12]. Second, we analyse our films by means of the Rutherford backscattering technique. This gives us another estimate of y and in addition, it shows that the homogeneity of our alloys is better than 5 % of y . Table I summarizes our data for the two alloys studied.

Table I. — *The composition, y , of samples as determined by several different methods, specified in the table. T_{cm} is the magnetic transition temperature.*

Quartz monitor (nominal y)	Extraordinary Hall coefficient		Rutherford backscattering
	T_{cm} (K)	y	
0.09	143	0.089 ± 0.002	0.086 ± 0.003
0.25	303	0.24 ± 0.01	0.23 ± 0.01

The deposited films were electrolytically hydrogenated at a temperature of about -80°C , directly inside the helium cryostat as described elsewhere [4, 13]. The charging procedure is controlled by monitoring the film resistance as a function of charging time. This resistance goes through a maximum and then drops to a final value which for the most Ni rich alloys ($y = 8$ and 25%) is lower than the initial resistance i.e. that for $x = 0$. We have not measured the deuterium concentration, x , but by considering the residual resistivity due to deuterium vacancies, and the residual resistivity of Ni in Pd and in PdD_x , we deduce that x is almost the same for all alloys and is close to $x = 1$. The exact value of x is not important in these studies, as will become evident in the following sections, but it is because we compare the change of T_c with that of the electron-optical phonon coupling parameter λ_{op} for the same deuterium concentration, x .

We prefer to use deuterium instead of hydrogen because there is a correspondingly larger contribution from optical phonon scattering to the resistivity in the temperature range, $50\text{ K} < T < 100\text{ K}$, for which there is no loss of D or H from our films, a few hundreds Å thick, (T_{max} on figure 1 represents the maximum temperature of our resistivity measurements).

3. Analysis of the experimental data. — The phonon electrical resistivity $\rho(T)$ and the superconducting transition temperature, T_c , can be written in the following way :

Fig. 1. — Experimental superconducting transition temperature T_c (1a), electron-optical phonon coupling parameter λ_{op} (1b) and $T_c(\lambda_{op})$ calculated from λ_{op} using the Mc Millan formula (1c), as a function of Ni concentration. All values are normalized to the corresponding value for $y = 0$.

$$\rho(T) = C \int \alpha_t^2 F(\omega) f\left(\frac{\hbar\omega}{kT}\right) d\omega, \quad (1)$$

$$T_c = \langle \omega \rangle \exp\left(-\frac{1}{g}\right), \quad g = \frac{\lambda}{1 + \lambda} - \mu^*,$$

$$\lambda = 2 \int \frac{\alpha_t^2 F(\omega)}{\omega} d\omega. \quad (2)$$

C is a constant involving the effective mass and the number density of conduction electrons, $F(\omega)$ is the phonon density of states, α_t^2 is a transport electron-phonon coupling matrix element which differs from the α^2 appearing in λ by a factor involving the scattering angle, and

$$f(x) = \frac{x}{(e^x - 1)(1 - e^{-x})}$$

is a statistical factor. The expression for T_c is the standard McMillan type formula.

At high enough temperatures $f(x) \simeq 1/x$ and $\rho(T) \simeq AT$ where A is proportional to

$$\lambda_t = 2 \int \frac{\alpha_t^2 F(\omega)}{\omega} d\omega \simeq \lambda.$$

Thus, it is possible to extract λ from the measured values of $\rho(T)$. However, for compounds like $\text{Pd}_{1-y}\text{Ni}_y\text{D}_x$ we have to consider contributions to $\rho(T)$ both from acoustic and optic phonons i.e.

$$\rho(T) = \rho_{ac}(T) + \rho_{op}(T) \quad (3)$$

and

$$\lambda = \lambda_{ac} + \lambda_{op}.$$

It is possible to separate the two contributions because at low enough temperatures ($T < 50\text{ K}$) only acoustical phonons are thermally excited, so that $\rho(T) = \rho_{ac}(T)$. Approximating $\rho(T)$ in this temperature range by a Grüneisen function,

$$\rho_{ac}(T) = \rho_G(T/\theta_{ac}, A_{ac}),$$

and assuming that this approximation is also valid at higher temperatures, it is possible to isolate the optical phonon contribution over the whole temperature interval considered i.e.

$$\rho_{\text{op}}(T) = \rho(T) - \rho_{\text{ac}}(T).$$

The optical contribution is then analysed by approximating the optical phonon spectrum with an Einstein spectrum i.e. $\rho_{\text{op}}(T) = \rho_E(T/\theta_{\text{op}}, A_{\text{op}})$. A best fit of $\rho_{\text{ac}}(T)$ and $\rho_{\text{op}}(T)$ with ρ_G and ρ_E permits us to determine θ_{ac} (the Debye temperature), θ_{op} (the Einstein temperature), A_{ac} and A_{op} . Since the constant C is not known precisely, one can determine only the ratio $\lambda_{\text{op}}/\lambda_{\text{ac}} = A_{\text{op}}/A_{\text{ac}}$. Absolute values of λ_{op} and λ_{ac} can nevertheless be obtained by calculating the corresponding values λ_{op}^0 and λ_{ac}^0 for the nickel free compound using relations (2) and (3), for which we assume $\mu^* = 0.1$, a typical value of the electron-electron repulsive interaction parameter in non transition metals and $\langle \omega \rangle = (\theta_{\text{ac}})^{\lambda_{\text{ac}}/\lambda} (\theta_{\text{op}})^{\lambda_{\text{op}}/\lambda}$.

4. Results and discussion. — Figure 1a shows the decrease of T_c with y for several deuterated samples including those two for which we have also measured the resistivities. These data are in good agreement with results obtained by Stritzker [9] and indicate that T_c approaches zero for a nickel concentration close to 13 %. No superconductivity has been observed in the $y = 25\%$ sample down to 1.1 K : this is again in agreement with the data of Stritzker but not with those of Skośkiiewicz [14, 9]. We have no explanation for this discrepancy. Following the procedure outlined above, we show in figure 2 the contribution $\rho_{\text{op}}(T)$ arising from optical phonon scattering for different Ni concentrations $y = (0, 0.09, 0.25)$. The procedure for separating the optical and acoustical phonon contributions is illustrated in this figure for the $y = 0$ case. At first sight one observes a decrease of $\rho_{\text{op}}(T)$ with y . The numerical analysis shows that one can obtain a good fit for $\rho_{\text{op}}(T)$ using an Einstein spectrum. This fit indicates that the decrease of $\rho_{\text{op}}(T)$ cannot be attributed to a hardening of the optical phonons. If the electron-phonon coupling parameter is written in the usual form

$$\lambda_{\text{op}} = \frac{\eta_{\text{op}}}{M\omega_{\text{op}}^2}$$

our data imply instead a decrease of η_{op} with y . The decrease of λ_{op} (normalized to λ_{op}^0 when $y = 0$) is shown in figure 1b (we have not drawn $\lambda_{\text{ac}}(y)$, which depends only slightly on y).

One can try to relate the change of λ_{op} with y with changes in the electronic band structure accompanying the replacement of Pd by Ni. Recent theoretical band structure calculations [15] made on pure PdH and NiH compounds show that η_{op} is sensitive primarily to the H site Fermi level density of states, and an important difference between PdH and NiH is that

Fig. 2. — Contributions to phonon resistivity arising from optical phonon scattering ($\cdots$) for different Ni concentrations y . To illustrate how the separation procedure described in the text works, the complete data for $y = 0$ are also shown. The acoustical contribution ($---$) is a theoretical Grüneisen law fitted to the low temperature resistivity. The optical contribution is obtained by subtracting the acoustical contribution from the experimental resistivity. The solid line represents the best fit to the data of the sum of the theoretical acoustic + optical contributions (see text).

the Fermi level is much closer to the top of the d band in NiH which will result in a lower type density of states at the H site for NiH compared to PdH. The calculated value of η_{op} is more than two times smaller for NiH and thus could possibly account for the observed decrease of λ_{op} with y .

However it is not certain that such a decrease in λ_{op} would lead to the observed large decrease of T_c . If one compares, for instance, the present data with those observed on PdD_x alloys [13] where there is a similar correlation between $T_c(x)$ and $\lambda_{\text{op}}(x)$, one finds that

$$\left| \frac{d\lambda_{\text{op}}(y)}{dT_c} \right| < \left| \frac{d\lambda_{\text{op}}(x)}{dT_c} \right|,$$

which means that the change of λ_{op} for a given change of T_c is smaller as a function of the nickel concentration y than as a function of the deuterium concentration x . To quantify this observation we calculate by how much T_c should decrease with y using the mea-

sured changes in λ_{op} (Fig. 1b). The calculated values of T_c are reported in figure 1c, and lie above the observed T_c points which suggests that part of the variation of $T_c(y)$ results from some other cause. First consider the acoustical contribution λ_{ac} ; experiments show that this term is small while theory [15] indicates that η_{ac} is similar in both PdH and NiH. Therefore this term is probably not relevant. A second possibility is some sort of magnetic contribution to the change of T_c . Ni is not magnetic in PdH in the sense that there is no local moment on the Ni atoms. However, it has been shown that transition metal impurities which do not form local moments produce nevertheless a depression of T_c , which is smaller than that for magnetic impurities, and which is related to the Coulomb repulsion between localized d electrons of opposite spins [16] or, possibly to localized magnetic fluctuations [16]. The calculated value of $\Delta T_c/T_c$ is expected to be of the order of 0.1 per percent of Ni, a value large enough to explain the observed decrease of T_c [16]. Note also that such a decrease of T_c is not observed for Pt which is iso-electronic to Ni but which shows a smaller tendency towards formation of magnetic moments than Ni. One can also argue that the tendency towards magnetism

which can be described by the value of the Kondo temperature, T_K , is more pronounced for the matrix PdH than for a classical monovalent matrix. For instance, Co impurities are non magnetic in Cu (very high T_K) whereas they are more magnetic in PdH_x (T_K in the range of 1 to 10 K) [17]. Finally note that a decrease of T_c of the same order of magnitude as in Pd_{1-y}Ni_yD_x alloys is also seen in the Al-Ni alloys [16, 18] despite the fact that d transition metal impurities form no magnetic moment in the Al matrix.

In conclusion we observe a large decrease in T_c with increasing nickel concentration in Pd_{1-y}Ni_yD_x alloys. Only a part of this variation can be attributed to a decrease of the coupling of electrons to the optical phonons and the total variation in $T_c(y)$ can only be explained if one includes some other effect related, most probably, to the magnetic structure of the Ni impurity. Tunnelling measurements on these same alloys are in progress to try to explain this problem.

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References

- [1] SKOŚKIÉWICZ, T., *Phys. Status Solidi* (a) **11** (1972) K 123.
- [2] STRITZKER, B., BUCKEL, W., *Z. Phys.* **257** (1972) 1.
- [3] EICHLER, A., WÜHL, H., STRITZKER, B., *Solid State Commun.* **17** (1975) 213.
- [4] DUMOULIN, L., NEDELLEC, P., ARZOUMANIAN, C., BURGER, J. P., *Phys. Status Solidi* (b) **90** (1978) 207.
- [5] MAC LACHLAN, D. S., MAILFERT, R., BURGER, J. P., SOUFFACHE, B., *Solid State Commun.* **17** (1975) 281.
- [6] GÓRSKA, A., GÓRSKI, A. M., IGALSON, J., PINDOR, A. J., ŚNIADOWER, L., *Proc. of 2nd Int. Congress « Hydrogen in Metals »*, Paris, 2A10 (1977).
- [7] PAPAConstantopoulos, D. A., KLEIN, B. M., *Phys. Rev. Lett.* **35** (1975) 110;
PAPAConstantopoulos, D. A., KLEIN, B. M., ECONOMOU E. N., BOYER, L. L., *Phys. Rev.* **B 17** (1978) 141.
- [8] STRITZKER, B., *Z. Phys.* **268** (1974) 261.
- [9] STRITZKER, B., WÜHL, H., in « Hydrogen in Metals », *Topics in Applied Physics*, Vol. **29** II (Springer Verlag) 1978, p. 243.
- [10] VAN DONGEN, T. M., MYDOSH, T. A., *Z. Phys. Chem.* **Bd 116** (1979) 149.
- [11] LANDOLT-BÖRNSTEIN, Springer Verlag II band 9 Teil : *Magnetische Eigenschaften I* (1962) 1-56.
- [12] CRANGLE, J., SCOTT, W. R., *J. Appl. Phys.* **36** (1965) 921.
- [13] ARZOUMANIAN, C., BURGER, J. P., DUMOULIN, L., NEDELLEC, P., *Z. Phys. Chem.* **116** (1979) 117.
- [14] SKOŚKIÉWICZ, T., *Proc. 5th Intern. Conf. High Pressure and Technology*, Moscow, 1975.
- [15] GUPTA, M., BURGER, J. P., *J. Phys. F*, in press.
- [16] KAISER, A. B., thesis work, University of London (1971).
- [17] SENOSSI, S., BURGER, J. P., SOUFFACHE, B., *Phys. Lett.* **54A** (1975) 288.
- [18] AOKI, R., OHTSUKA, T., *J. Phys. Soc. Japan.* **23** (1967) 955 ; **26** (1969) 651.