SPECIFIC HEAT AND SUSCEPTIBILITY ENHANCEMENT IN DILUTE Pd:Ni ALLOYS

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This paper deals with a study of dilute Pd:Ni alloys, by magnetization and specific-heat measurements on the same samples. As is known, the Stoner enhancement factor of the susceptibility of Pd is very large. Recent theoretical investigations[1-3] have shown that the interactions between spin fluctuations and d electrons result in an increase of the effective electron mass and, consequently, the electronic specific heat. It is therefore particularly interesting to introduce Ni into Pd if it appears that its presence in the alloy increases the susceptibility above that of pure Pd without the Ni itself having a magnetic moment.

In 1962, Bozorth, Davis, and Wernick[4] showed that, in contrast to the Pd:Fe and Pd:Co alloys, the paramagnetic Curie temperature of Pd:Ni becomes zero for concentration lower than 2.25%. The study of the saturation magnetization of concentrated Pd:Ni alloys[5-7] allowed us to estimate that the magnetic moment of Ni vanishes near 2% concentration. Shaltiel et al.[8] have shown that the Curie-Weiss law is not obeyed below 2% Ni and that the Ni increases the Pd susceptibility. But since their alloys probably contained impurities possessing their own magnetic moments, it is difficult to divide the total susceptibility they measured into the various contributions. This is the reason why we measured the magnetization of Pd:Ni alloys in fields[9] up to 35 kOe and temperatures ranging from 0.05 to 4°K, studying the disappearance of the magnetic moment and the enhancement of the paramagnetic susceptibility.

All our samples were melted for one hour at 1650°C in a vacuum furnace in Al_2O_3 crucibles. Some of them were quenched in oil after annealing in vacuo at 900°C. No difference was found between the annealed and quenched and the untreated samples which we attribute to the excellent solubility of Ni in Pd.

The samples obtained in this way were used in their entiretry to measure the specific heat as well as the susceptibility. They were in the form of cylinders of 20 mm in length and 7 mm diam, weighing about 10 g. A small piece was cut from one end for analysis and to obtain a clean straight surface to assure a good thermal contact between the cooling part of the cryostat and the sample.[9]

High-precision spectroscopic analysis of several samples showed no significant difference (a few percent relatively) between the real and the nominal atomic concentrations. After some final investigations the samples will be analyzed completely, but we are already quite sure that the nominal concentration indicates well enough the real concentrations simply because the whole ingot was used for the measurements.

The magnetization has been measured as a function of the external field H for different temperatures. From the linear part of the curves at high fields and temperatures below 2°K, one can split the magnetization into two terms:

$$\sigma = \sigma_m(H, T, c) + \chi(c)H.$$

σ_m saturates easily at $\sigma_S(c)$ for any concentration c if $H > 20$ kOe in the least favorable case and $T < 2$°K. $\chi(c)$ is independent of the external field. It represents the paramagnetic susceptibility and is independent of temperature ($T < 2$°K). Below 1.5% Ni (Table I), $\sigma(c)$ becomes a constant corresponding to about the saturation magnetization of 70 ppm Fe (Table I). (The system Pd:Fe will be the subject of a different paper.[10]) Most of this impurity is introduced by the use of Al_2O_3 crucibles, since pure Pd as received does not show the same effect until it is melted itself in such a crucible. The introduction of Fe during the melting seems rather reproducible. Above 1.5% Ni the saturation magnetization increases rapidly with concentration, thus showing the presence of magnetic Ni atoms.

The relative increase of the paramagnetic susceptibility, $\Delta\chi/\chi_{Pd}$, with Ni concentration (Fig. 1) rises up to a maximum of 4 at 2.5% Ni and then decreases again (Table I). This decrease in the ferromagnetic region has already been observed in the Pd:Fe system.[11]

We also measured the specific heat of the same samples between 0.3 and 3°K using a cryostat described elsewhere.[12] The results can be represented[13] by $C = \gamma T + \beta T^3$. In particular no evidence was found for a term $T^3 \ln(T/T_F)$.[14] The relative increase of the electronic specif-

Table I. $\chi_F = (dM/dh)$ is the paramagnetic susceptibility of Pd:Ni alloys at $h > 20$ kOe and $T = 0.1°K$; σ_s the saturation magnetization. The error on the electronic specific-heat coefficient γ is estimated to be ±0.5%.

Ni concentration (at.%)	$10^6\chi_F$ (emu g^{-1})	$\Delta\chi_F/\chi_{Pd}$	σ_s (emu g^{-1})	γ (mJ $mole^{-1}$ deg^{-2})	$\Delta\gamma/\gamma_{Pd}$
0	7.0 ±0.01	0	0.035 ±0.004	9.40	0
0.2	8.44 ±0.1	0.21 ±0.02	0.026 ±0.003	9.89	0.052
0.35	8.80 ±0.15	0.26 ±0.02	0.036 ±0.004	9.96	0.0595
0.5	10.15 ±0.15	0.45 ±0.02	0.035 ±0.004	10.26	0.0915
1	15.55 ±0.3	1.22 ±0.02	0.042 ±0.005	11.14	0.185
1.5	22.9 ±0.3	2.27 ±0.05	0.080 ±0.008	12.43	0.32
2	28.0 ±0.4	3.00 ±0.06	0.515 ±0.01	13.12	0.395
2.5	33.3 ±0.6	3.76 ±0.09	1.17 ±0.02	14.76	0.570
3	32.4 ±0.6	3.63 ±0.09	2.20 ±0.04	15.13	0.610
5	17.8 ±1.6	1.54 ±0.23	6.44 ±0.06	13.46	0.430
10	6.8 ±2.4	−0.03 ±0.3	13.40 ±0.07	11.88	0.265

ic heat, $\Delta\gamma/\gamma_{Pd}$, is plotted against concentration in Fig. 1, where it can be seen to be of the same form as $\Delta\chi/\chi_{Pd}$ though much smaller (Table I). Below 0.5% we find the following expressions:

$$\frac{1}{\chi_{Pd}}\frac{\Delta\chi}{\Delta c} \simeq 87; \quad \frac{1}{\gamma_{Pd}}\frac{\Delta\gamma}{\Delta c} \simeq 15.$$

Between 0.5 and 1.5% the results indicate that there are some interactions between nickel atoms. Above 1.5% the σ_s curve shows the effect of these interactions; certain impurities become magnetic.[15]

The specific-heat results seem to be in agreement with those from Schindler et al.,[16] who found in addition an electrical resistivity term $A(c)T^2$ with $(1/A)(dA/dc) \simeq 750$. These properties can be interpreted as an increase of the value of the intra-atomic Coulomb interaction with respect to that in pure Pd. Lederer and Mills[17] developed a theory which relies upon this increase being localized near the Ni atoms. The Ni atoms, being nearly magnetic, enhance the spin polarization and the amplitude of the spin fluctuations in their near neighborhood. Using this theory we could compute directly the properties of Pd from the ratio

$$\frac{\gamma_{Pd}}{\chi_{Pd}}\frac{\Delta\chi}{\Delta\gamma} = \frac{87}{15} = 5.8$$

because this ratio is equal to $\alpha_0\rho^*/3\rho$, ρ^*/ρ being the ratio of the enhanced density of states deduced from specific heat data to the bare density of states, and α_0 being the enhancement parameter of the matrix:

$$\alpha_0 = \frac{\rho^*}{\rho}\frac{\chi_{Pd}}{\chi_{sh}},$$

where χ_{Pd} is the measured susceptibility of the matrix and χ_{sh} a susceptibility deduced from the specific heat data of Pd using the free-electron model.

From our measurements we find $\chi_{Pd}/\chi_{sh} = 5.8$; and then, from the preceding formulas,

$$\rho^*/\rho = 1.73; \quad \alpha_0 = 10.$$

Finally, we can compute theoretical values

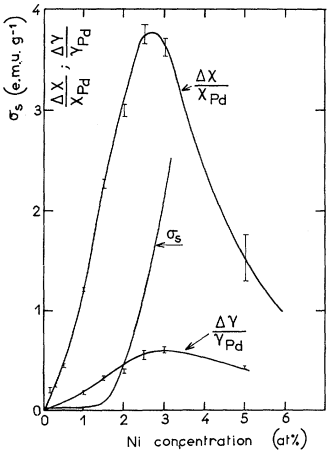

FIG. 1. The increase of the electronic specific heat of Pd:Ni alloys $(\gamma_{Pd:Ni}-\gamma_{Pd})/\gamma_{Pd} = \Delta\gamma/\gamma_{Pd}$; the increase of the paramagnetic susceptibility $(\chi_{Pd:Ni}-\chi_{Pd})/\chi_{Pd} = \Delta\chi/\chi_{Pd}$; the saturation magnetization σ_s as a function of Ni concentration.

for $\Delta\gamma$, $\Delta\chi$, and A at low concentrations from the Lederer and Mills theory which are in good agreement with the experimental value. The ρ^*/ρ ratio seems quite reasonable.[3,18,19] Another fact seems to support the theory of the localized enhancements.[15,16] Although the mean increase of the susceptibility is high, the moment of the Fe impurities does not change with Ni concentration. This can be understood only by a localized increase of χ in the neighborhood of the Ni atoms.

We could obtain some data for the coefficient of the T^3 term of the specific heat, in spite of the small value of the ratio $\beta T^3/\gamma T$ even at 3°K. Although further investigations are under way to lower the error in β, we can already say that there is a steady increase of the calculated Debye temperature Θ_D with concentration; but our results do not determine whether it is a new βT^3 term or whether it is a real variation of Θ_D.

For high concentrations, Θ_D falls off again and at 10% it is approximately the same as for our pure Pd (235 ± 8°K). This behavior cannot be explained by a mass effect but rather by the magnetic fluctuations or perhaps by a phonon-paramagnon coupling.[20]

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THERMAL AND MAGNETIC DEGRADATION OF THE QUASIBOUND STATE IN DILUTE MAGNETIC COPPER-CHROMIUM ALLOYS*

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Recent theories of the low-temperature electron state in dilute alloys of magnetic transition-metal atoms in simple metallic hosts have treated the scattering of itinerant electrons as predominantly s wave.[1-3] For this reason, the increase in resistivity with decreasing temperature as the low-temperature state is formed is limited to approximately one s-wave unitarity limit, or about 0.38 nΩ cm per (at.) ppm impurity in copper. Within the framework of these theories, there has also been quite a bit of recent interest in the behavior of the vari-