Giant moments in paramagnetic Pd-Ni alloys

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The magnetizations of several paramagnetic Pd-Ni alloys were measured between 2.4 and 100 °K in fields up to 56 kOe. For the alloys of up to ~1.8-at.% Ni, it is deduced from the high-field and low-field behavior that stable giant moments ($\sim 18\mu_B$) are nucleated by groups of three or more nearest-neighbor Ni atoms. However, the spin number associated with each giant-moment complex is quite small (~2). The isolated Ni atoms and the nearest-neighbor Ni pairs simply make large exchange-enhanced contributions to a relatively temperature-independent component of the susceptibility. At a higher Ni concentration (~1.9 at.%), a departure from this simple situation is seen to emerge.

I. INTRODUCTION

The alloys of Pd-Ni occupy a strategic position in the broad spectrum of magnetic solid-solution alloys. Whereas isolated impurity atoms of Fe and Co form stable local moments in a variety of nonmagnetic metal hosts, there is no analogous situation known in the case of Ni. When the metal host is Pd, whose susceptibility is highly exchange enhanced, the formation of local moments on Fe or Co impurity atoms is accompanied and assisted by the induced magnetic polarization of the neighboring Pd atoms, giving rise to giant-moment complexes with a Curie-Weiss-like susceptibility.[1] Yet even in Pd, isolated Ni atoms do not exhibit stable local moments; instead, they make local exchange-enhanced contributions to the susceptibility, which remains fairly constant (Pauli-like) at low temperatures.[2] However, stable magnetic moments do occur in concentrated paramagnetic alloys of Ni with Cu,[3,4] V,[5] or Rh,[6] where giant moments are nucleated at those Ni atoms with extremely Ni-rich local environments. Thus, it seems reasonable to expect even stronger local-environment effects on stable moment formation in paramagnetic Pd-Ni, where the critical Ni concentration for ferromagnetism[7] (~2.5 at.%) is much lower than in any of the above systems. Indeed, from a recent susceptibility study of paramagnetic Pd-Ni alloys, it was concluded that groups of three or more nearest-neighbor Ni atoms may be playing a magnetic role similar to that of isolated Fe or Co atoms in the same Pd host.[8] However, the data analysis that led to this conclusion was described cursorily and only for one alloy (of ~1.5-at.% Ni).

In this paper, we present our detailed experimental results for the magnetization-field-temperature properties of several paramagnetic Pd-Ni alloys. For the alloys of up to ~1.8-at.% Ni, we deduce fairly unambiguously that stable giant moments are produced by groups of at least three nearest-neighbor Ni atoms. However, the spin number associated with each giant-moment complex is anomalously small. The isolated Ni atoms and the nearest-neighbor Ni pairs simply contribute to a relatively temperature-independent component of the susceptibility, the contributions of the latter being especially large. At a higher Ni concentration (~1.9 at.%), a departure from this simple situation begins to emerge.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Our Pd-Ni alloy samples were cut as cylinders (3 mm in diameter, 6 mm long) from buttons prepared by the arc melting of 99.995% pure metals under argon. They were then annealed for 5 days at 1000 °C and water quenched. Their magnetizations were measured with a vibrating-sample magnetometer between 2.4 and 100 °K in fields from 56 kOe down to 20 Oe.

The magnetization-field (σ-H) curves obtained at 2.4 °K for the alloy samples and a pure Pd sample are displayed in Fig. 1. Compared to the curve for Pd, which is essentially linear at all fields, the curves for the alloys rise more rapidly with a distinct concave-downward curvature, which becomes more pronounced as the Ni concentration increases. In all cases, however, the curvature diminishes at high fields and is almost absent above ~30 kOe. Thus, the high-field portion of each σ-H curve may be expressed as

$$\sigma = \sigma_0 + \chi' H \quad , \tag{1}$$

where χ' is allowed to have a mild dependence on H. The high-field slopes of the curves, determined at 50 kOe, were constant below ~10 °K and are therefore representative of zero temperature. Their values are listed under $\chi'_{HF}(0)$ in Table I. We note that the $\chi'_{HF}(0)$ values for the alloys are substantially higher than that of pure Pd and rise steadily with increasing

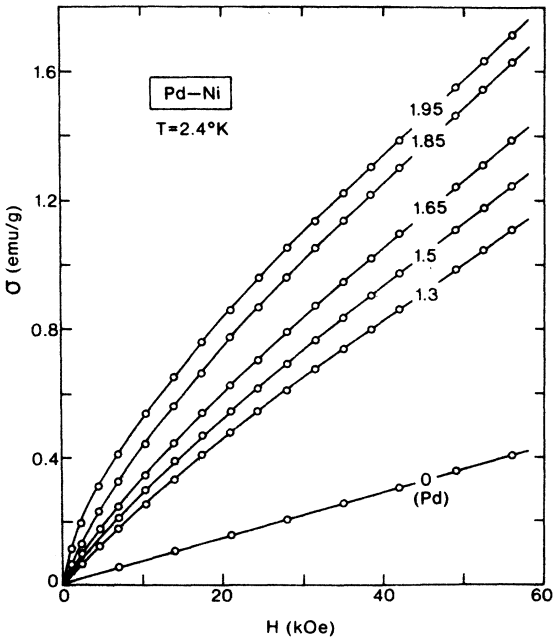

FIG. 1. Magnetization vs field at 2.4 °K for Pd-Ni alloys of various compositions (in at.% Ni).

Ni concentration up to 1.95 at.%, where there appears to be a small decrease. Later comparison of these results with those at low fields will allow us to estimate the field dependence of χ' and thus obtain extrapolated values for the σ_0 in Eq. (1).

From the zero-field slopes of the σ-H curves at various temperatures, the initial susceptibilities (χ_0) were determined for each alloy. Their reciprocals are plotted against temperature in Fig. 2(a). These plots, in their characteristic concave-downward curvature at low temperatures, resemble the analogous plots obtained earlier for Ni-Cu,[4] Ni-V,[5] and Ni-Rh,[6] where it was found that χ_0 was resolvable into a Curie-Weiss-like component (χ_{CW}) and a relatively temperature-independent component (χ'). We therefore assumed that similarly for the Pd-Ni alloys,

$$\chi_0 = \chi_{CW} + \chi'(T), \quad \chi_{CW} = C_{CW}/(T-\Theta) \ . \tag{2}$$

Making the additional assumption that χ' has a constant value $\chi'_{LF}(0)$ at low temperatures, we achieved an excellent data fit to Eq. (2) for each alloy up to ~10 °K. With the C_{CW} and Θ values obtained from this low-temperature fit, we extended χ_{CW} up to the higher temperatures of measurement [as shown for χ_{CW}^{-1} in Fig. 2(b)], subtracted it from the measured χ_0, and thus determined $\chi'(T)$, whose reciprocals are plotted in Fig. 2(c).

The values for C_{CW}, Θ, and $\chi'_{LF}(0)$ extracted from this data analysis are listed in Table I. Clearly, there is very good overall agreement between the values of $\chi'_{LF}(0)$ and $\chi'_{HF}(0)$. This agreement strongly supports the validity of Eqs. (1) and (2) and their implication that Pd-Ni alloys have stable magnetic moments (whose saturation magnetization and susceptibility are σ_0 and χ_{CW}) as well as induced magnetic moments (with susceptibility χ'). In closer detail, the values of $\chi'_{HF}(0)$ are seen to lie consistently just below those of $\chi'_{LF}(0)$. Although their differences may in part be an artifact of our data analysis, they were taken to be indicative of a small field dependence of $\chi'(0)$. Making the reasonable assumption that $\chi'(0)$ has the form $\chi'_{LF}(0) - \alpha H^2$, and evaluating the coefficient α from $\chi'_{LF}(0) - \chi'_{HF}(0)$, we determined the magnetization

$$\sigma' = \chi'_{LF}(0)H - \tfrac{1}{3}\alpha H^3 \ ,$$

which is represented schematically in Eq. (1) by the term $\chi'H$. Matching σ' to the high-field portion of each curve in Fig. 1, we extrapolated back to zero field and obtained a reliable value for σ_0. The σ_0 values for the alloys are listed in Table I. Also listed are the σ_0 and C_{CW} values obtained similarly for our Pd sample, which can be ascribed to a superparamagnetic (probably Fe) impurity of ~20 ppm.

If the stable magnetic moments in the Pd-Ni alloys, in excess of those introduced by the impurities in the Pd host, are ascribed to superparamagnetic entities of

TABLE I. Magnetic and concentration parameters for Pd-Ni alloys.

Alloy (at.% Ni)	$\chi'_{HF}(0)$[a]	$\chi'_{LF}(0)$[a]	Θ (°K)	C_{CW}[a]	σ_0 (emu/g)	$10^7 c_{3+}$	$10^6 c_2$	$10^5 c_1$
0 (Pd)	6.9	6.9	0	8.8	0.011	0	0	0
1.3	17.4	17.9	−2	56.8	0.091	851	801	1111
1.5	19.4	20.2	−2	75.5	0.128	1256	1028	1251
1.65	21.1	22.3	−2	101	0.166	1620	1211	1351
1.85	23.7	25.4	−2	146	0.243	2191	1467	1479
1.95	23.5	23.8	0	223	0.385	2513	1601	1540

[a] $\chi'_{HF}(0)$ and $\chi'_{LF}(0)$ in units of 10^{-6} emu/g Oe; C_{CW} in units of 10^{-6} emu K/g Oe.

concentration c^* and total moment μ^*, we may express σ_0 and C_{CW} for the alloy samples as

$$\sigma_0 = \sigma_0(\text{Pd}) + Nc^*\mu^* \quad , \tag{3a}$$

$$C_{CW} = C_{CW}(\text{Pd}) + Nc^*(S+1)\mu^{*2}/3Sk \quad , \tag{3b}$$

where N is the number of atoms per gram, k the Boltzmann constant, and S the spin number, such that $\mu^* = g_{\text{eff}}S$, in terms of an effective g factor. Furthermore, as a test of the previous report of stable moments in Pd-Ni,[8] we identify c^* with c_{3+}, the concentration of groups of three or more Ni atoms joined by nearest-neighbor bonds; calculated values of c_{3+} for our random Pd-Ni alloys[9,10] are listed in Table I. Then, according to Eqs. (3a) and (3b), both σ_0 and C_{CW} should vary linearly with c_{3+} from their values for "pure" Pd ($c_{3+}=0$). In Fig. 3, our results for σ_0 and C_{CW} are plotted versus c_{3+} and give a definite confirmation of this linear dependence for Ni concentrations up to ~1.8 at.%, above which there is a noticeable deviation. Quantitatively, by applying Eq. (3a) to the linear region of σ_0 vs c_{3+}, we find that $\mu^* = 17.8(\pm 0.2)\mu_B$. Inserting this μ^* value into Eq. (3b), we obtain various straight lines for C_{CW} vs c_{3+}, depending on the value of S, as shown in Fig. 3. The line that best fits our results within the linear region corresponds to $S=2$, which differs significantly from the spin value of ~24 given in the earlier report.[8]

The giant moment of $\sim 18\mu_B$ associated with each nearest-neighbor Ni triad (or larger group) in dilute *Pd*Ni must contain to a major extent the induced magnetic polarization of the Pd atoms (plus the isolated Ni atoms and nearest-neighbor Ni pairs) in the vicinity of the Ni triads. Thus, each nearest-neighbor Ni triad

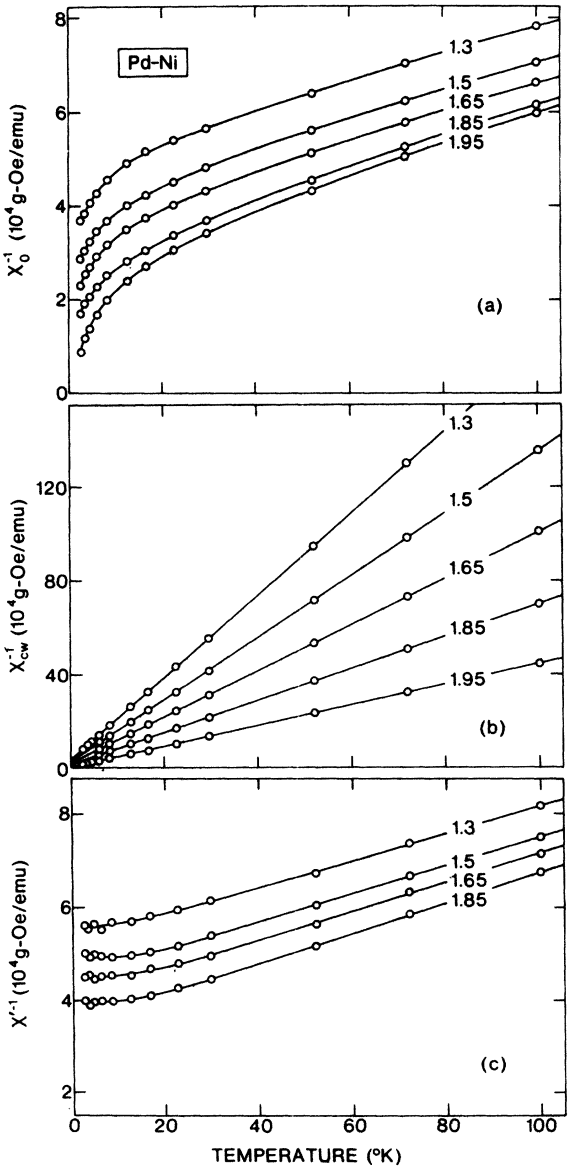

FIG. 2. Temperature dependence of (a) inverse initial susceptibility χ_0^{-1}, (b) χ_{CW}^{-1}, and (c) χ'^{-1}, where $\chi_{CW} + \chi' = \chi_0$, for Pd-Ni alloys of various compositions (in at.% Ni).

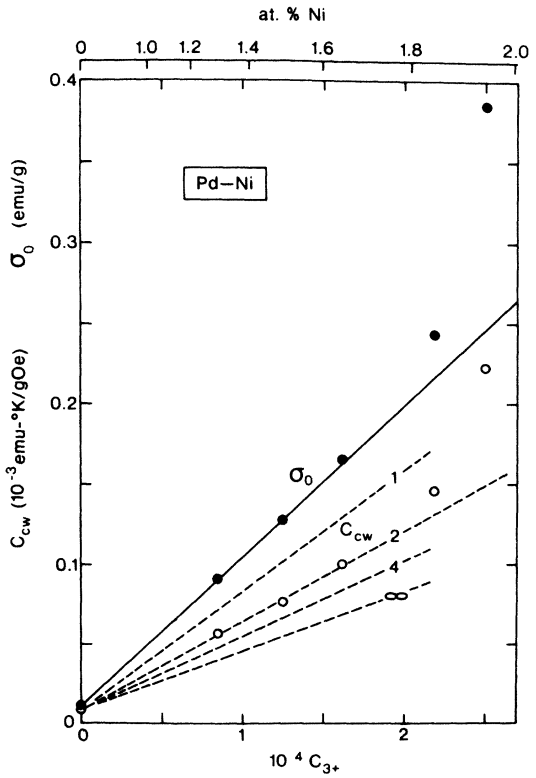

FIG. 3. σ_0 vs c_{3+} (closed circles) and C_{CW} vs c_{3+} (open circles) derived experimentally for various Pd-Ni alloys. Solid line for σ_0 vs c_{3+} corresponds to $\mu^* = 17.8\mu_B$; dashed lines for C_{CW} vs c_{3+} correspond to $\mu^* = 17.8\mu_B$ and different values of S (as labeled).

forms the nucleus of a superparamagnetic complex, which is analogous to the magnetic role of an isolated Fe or Co atom in Pd. Moreover, the spin value of 2, deduced for these giant-moment complexes (corresponding to an anomalously high g_{eff} value of ~ 9) suggests that the only spin degrees of freedom are essentially those of the Ni triads, with little contribution from the surrounding polarization clouds. This situation is also analogous to that of dilute Fe or Co in Pd, where the spin value deduced from specific heat data is anomalously small [11] Regarding the stability of the giant moments in dilute *Pd*Ni, it is very plausible that the constant Θ value of -2 °K (see Table I) signifies a spin-fluctuation temperature of ~ 2 °K, although other factors (exchange, anisotropy, etc.) cannot be ruled out.

Aside from the very small fraction included in the polarization clouds around the nearest-neighbor Ni triads, the isolated Ni atoms and nearest-neighbor Ni pairs in dilute *Pd*Ni are undoubtedly contributing to the relatively temperature-independent susceptibility (χ'), which rises with increasing Ni concentration. Hence, consistent with the analysis of the earlier report,[8] we express the low temperature χ' for the alloys as

$$\chi'(0) = (1 - c_1 - 2c_2)\chi_{\text{Pd}}'(0) + c_1\chi_1'(0) + c_2\chi_2'(0) \quad , \tag{4}$$

where $\chi_1'(0)$ and $\chi_2'(0)$ are the susceptibility contributions of the isolated Ni atoms and nearest-neighbor Ni pairs, respectively, whose concentrations in our alloy samples (c_1 and c_2)[10] are listed in Table I. Applying Eq. (4) to the $\chi'_{11}(0)$ results given in the table, we obtain a very good fit with $\chi_1'(0) = 3.5 \times 10^{-4}$ emu/g Oe and $\chi_2'(0) = 90 \times 10^{-4}$ emu/g Oe, for all the alloys up through 1.85-at.% Ni. These values agree roughly with those given in the previous report[8] and correspond to $6.6 \times 10^{-6}\mu_B$/Oe for an isolated Ni atom and $170 \times 10^{-6}\mu_B$/Oe for a nearest-neighbor Ni pair. These susceptibility contributions are far greater than that of a Pd atom ($0.13 \times 10^{-6}\mu_B$/Oe) and thus represent local exchange enhancements that are extremely high. In fact, according to the value for $\chi_2'(0)$, our maximum available field of 56 kOe will induce a magnetic moment per nearest-neighbor Ni pair of nearly $10\mu_B$. This induced giant moment must derive in large part from the Pd (and isolated Ni) atoms in the vicinity of the Ni pairs. It should also be noted that the spin-fluctuation temperature of a nearest-neighbor Ni pair is at least 10 °K, which we estimate from the low-temperature shape of the $\chi'^{-1}(T)$ curves in Fig. 2(c), the contributions to χ' from the Pd and isolated Ni atoms being fairly constant. A more detailed analysis of our $\chi'(T)$ results will be given in a future report.

In the present discussion, we have shown that Pd-Ni alloys of up to ~ 1.8-at.% Ni are characterized magnetically by a few well-defined local states involving small groups of Ni solute atoms and the neighboring parts of the Pd host. At a higher Ni concentration (~ 1.9 at.%), our experimental results for various parameters [σ_0, C_{CW}, $\chi'(0)$, and Θ, as shown in Fig. 3 and Table I] all indicate the beginning of a deviation from this simple behavior. Our Pd-Ni study is currently being extended to even higher Ni concentrations, up through the critical concentration into the weakly ferromagnetic regime, where giant polarization clouds have been observed in neutron scattering experiments[12]; the results will be presented in a later report.

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[9]Pd-Ni being a highly miscible system and the alloys studied fairly dilute, the rapid quenching of our samples from 1000 °C is assumed to have preserved an almost perfect atomic disorder.

[10]For random binary systems of composition $A_{1-c}B_c$ and various simple structures (including the fcc structure of Pd-Ni), expressions are given by R. E. Behringer [J. Chem. Phys. 29, 537 (1958)] for the concentrations of groups of two and three nearest-neighbor B atoms (c_2 and c_3) and of isolated B atoms (c_1). To determine $c_{3,\ell}$, we

extended these considerations to groups of four B nearest neighbors in a fcc structure and obtained for their approximate concentration: $c_4 \approx 220x^4(1-x)^{30}$. For $x \leq 0.02$, this gives $c_4 \lesssim 0.08c_3$, and since the concentrations of larger groups are negligible ($<0.01c_3$), we take c_{3+} to be $c_3 + c_4$.

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