GIANT MOMENTS IN Pd(Ni) ALLOYS NEAR THE CRITICAL COMPOSITION*

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Neutron-scattering experiments show evidence of long-range magnetic polarization of the palladium matrix in dilute ferromagnetic Pd(Ni) alloys. The measured cross sections, for alloys containing up to 4.7 at.% nickel, are interpreted in terms of a model in which the concentration of ferromagnetically aligned giant moments is less than the concentration of nickel atoms.

Evidence will be presented for the existence of long-range magnetic polarization of the palladium matrix in ferromagnetic Pd(Ni) alloys. The magnetization measurements of Crangle and Scott[1] and Chouteau et al.[2] indicate that the critical concentration for the onset of ferromagnetism in this system is slightly less that 2 at.% nickel.[3] The moment per added nickel atom is about $4\mu_B$ between 2 and 5.5% nickel, but decreases at higher concentrations. In contrast, the critical concentration for Pd(Fe) and Pd(Co) alloys is less than 0.1%,[1,4] and the moment per solute atom is about $(10\text{ to }12)\mu_B$ in very dilute alloys but begins to decrease at solute concentrations as low as 1%. Low, Holden, and Hicks[5,6] have shown, from neutron-scattering measurements, that the polarization of the palladium matrix in dilute Pd(Fe) and Pd(Co) alloys extends to a distance of about 10 Å from the solute atoms, and the present experiment was undertaken to investigate the moment distribution in dilute Pd(Ni) alloys.

Polycrystalline alloy specimens containing 3.0, 3.4, 4.7, and 6.3% nickel were prepared by powder metallurgy from palladium and nickel of spectrographic purity and were homogenized by annealing at 1200°C for 12 h. Traces of iron and cobalt were present in the alloys but their atomic concentrations were less than 45 ppm in all except the 4.7% alloy, which had a cobalt concentration of 190 ppm. Measurements of the elastic diffuse magnetic scattering of neutrons of 4.8-Å mean wavelength were made at 4.2°K by using the technique described by Low and Holden.[5] The measured angular distributions are presented in Fig. 1, and all show strong forward peaks that are characteristic of scattering from widespread polarization distributions in the palladium matrix. The polarization distributions associated with the iron and cobalt impurity atoms were assumed to produce the same scattering in the Pd(Ni) alloys as in the respective Pd(Fe) and Pd(Co) alloys. This scattering averaged about 6% of the total measured intensities and was subtracted from the observed angular distributions before performing the analysis described below.

The cross section for the elastic magnetic diffuse scattering of neutrons by a random array of ferromagnetically aligned magnetic impurities is expressed,[5] for the magnetic field geometry used in this experiment, by

$$d\sigma/d\Omega = 0.049c(1-c)\left|\int \rho'(\vec{r})e^{i\vec{K}\cdot\vec{r}}d\vec{r}\right|^2 \quad \text{b/sr atom,} \qquad (1)$$

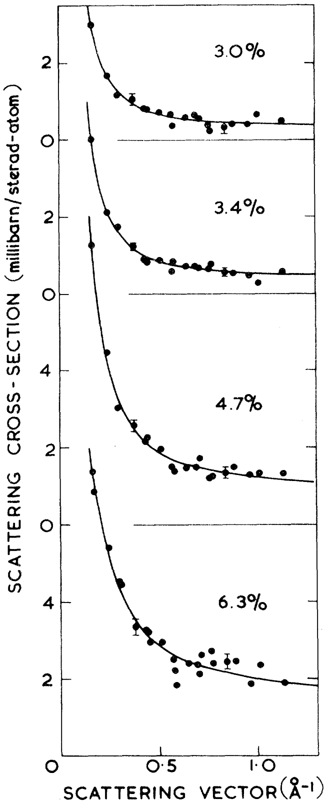

FIG. 1. Diffuse magnetic cross sections for the scattering of neutrons of 4.8-Å mean wavelength by four ferromagnetic Pd(Ni) alloys of given nickel concentrations at 4.2°K. The curves are fits of a form factor, which is the sum of form factors due to the nickel 3d moment and to the long-range polarization induced in the palladium matrix.

where c is the fractional impurity concentration, $\rho'(\vec{r})$ is the moment disturbance due to an impurity at the lattice site $r=0$, and $\vec{\kappa}$ is the neutron-scattering vector. The integration is taken over the volume of the specimen. For the forward direction,[7]

$$(d\sigma/d\Omega)_{\kappa=0}=0.049c(1-c)(d\bar{\mu}^2/dc) \quad \text{b/sr atom,} \tag{2}$$

where $\bar{\mu}$ is the mean moment per alloy atom in Bohr magnetons. These expressions are valid only if the moment disturbance produced by each additional impurity is independent of the disturbances already present. This condition obviously does not apply for dilute Pd(Ni) alloys which have a critical concentration for the onset of ferromagnetism. In order to use expressions (1) and (2), we shall assume, therefore, that dilute Pd(Ni) alloys can be described by a model in which the magnetic diffuse scattering originates from an array of identical moment disturbances whose concentration c^* is less than the nickel concentration c. We shall assume also that c^* increases steadily from zero as the nickel concentration increases beyond the critical concentration. This could describe, for example, a situation in which statistical fluctuations in the environment of the nickel atoms cause only a proportion of them to produce separate aligned polarization distributions. A similar model has been used successfully to account for diffuse neutron-scattering measurements on Ni-Cu alloys near the critical composition.[8]

With this model, Eqs. (1) and (2) may be rewritten[5] as follows:

$$d\sigma/d\Omega=0.049c^*(1-c^*)\,|M'(i)f_i(\vec{\kappa})+M'(h)f_h(\vec{\kappa})|^2 \quad \text{b/sr atom} \tag{3}$$

$$=|Af_i(\vec{\kappa})+Bf_h(\vec{\kappa})|^2, \tag{4}$$

and

$$(d\sigma/d\Omega)_{\kappa=0}=0.049c^*(1-c^*)\{M'(i)+M'(h)\}^2 \quad \text{b/sr atom} \tag{5}$$

$$=0.049c^*(1-c^*)\{M'(t)\}^2 \quad \text{b/sr atom,} \tag{6}$$

where $M'(i)$, $M'(h)$, and $M'(t)$ are, respectively, the $3d$ moment on the impurity atom, the moment induced in the palladium host by each impurity, and the total moment per impurity atom, all expressed in Bohr magnetons, and $f_i(\vec{\kappa})$ and $f_h(\vec{\kappa})$ are the form factors corresponding to $M'(i)$ and $M'(h)$. Low and Holden[5] conclude, from a discussion of the generalized susceptibility of the palladium matrix, that $f_h(\vec{\kappa})$ is of the form $1/(1+\vec{\kappa}^2/\vec{\kappa}_1^{\,2})$, corresponding to a polarization distribution of the form $e^{-\vec{\kappa}_1\cdot\vec{r}}/r$. The $3d$ form factor for nickel[9] may be approximated to sufficient accuracy by the expression $1-0.04\vec{\kappa}^2$ where $\vec{\kappa}$ is expressed in Å^{-1}.

Equation (4) was fitted to the experimental data for each specimen, treating A, B, and κ_1 as disposable parameters. The best values of the parameters for each specimen are listed in Table I, and the fitted curves are shown in Fig. 1. Table I also includes values of the forward scattering cross section that have been extrapolated from the fits to the experimental data.

The extrapolated forward cross section increases with increasing nickel concentration up to 4.7% Ni. For the 6.3%-Ni alloy the sharp decrease in the extrapolated cross section and the change in shape of the angular distribution, indicated by the increase in κ_1, suggest that nonlinear superposition of overlapping moment distributions is taking place. Saturation effects are also evident in the concentration dependence of the magnetization of Pd(Ni) alloys above about 5.5% Ni.[1,2] In contrast, nonlinear effects at solute concentrations as low as 1% are evident in the magnetization[1,4] and in the diffuse scattering angular distributions[5] of Pd(Fe) and Pd(Co) al-

Table I. Analysis of the measured diffuse magnetic neutron-scattering cross sections of ferromagnetic Pd(Ni) alloys in terms of Eq. (4). c is the nickel concentration, κ_1 is the fitted value of the inverse-range parameter, and the fitted parameters A and B are proportional to the nickel $3d$ moment and the palladium matrix moment per nickel atom, respectively. The extrapolated value of the forward cross section $(d\sigma/d\Omega)_{\kappa=0}$ is equal to $(A+B)^2$.

c (at.% Ni)	κ_1 (Å^{-1})	A (b/sr atom)$^{1/2}$	B	$\left.\frac{d\sigma}{d\Omega}\right\vert_{\kappa=0}^{\text{extrap}}$ (b/sr atom)
3.0	0.15	0.018	0.077	0.009
3.4	0.15	0.021	0.098	0.014
4.7	0.15	0.033	0.114	0.021
6.3	0.21	0.043	0.068	0.012
Representative error	±0.03	±0.014	±0.016	±0.004

loys. The saturation effects presumably occur at different concentrations because an iron or cobalt atom exerts a larger driving force on the palladium matrix than a nickel atom. As a result, the mean moment per atom of the palladium matrix approaches the saturation value of $0.36\mu_B$ more rapidly with solute concentration in Pd(Fe) and Pd(Co) alloys than in Pd(Ni) alloys. The range of the matrix polarization in the three most dilute Pd(Ni) alloys is similar to, but somewhat larger than, that in dilute Pd(Fe) and Pd(Co) alloys which have a reciprocal range parameter κ_1 just over 0.2 Å^{-1}.[6,10]

Within experimental error, the extrapolated forward cross sections of the three most dilute alloys are proportional to the difference $c-c_F$ between the nickel concentration c and the critical concentration c_F (about 2% nickel). Thus, ignoring the variation of the factor $1-c^*$ with concentration, it follows from Eq. (6) that the quantity $c^*\{M'(t)\}^2$ varies as $c-c_F$. The quantity $c^*M'(t)$ is equal to the mean moment per atom of alloy $\bar{\mu}$, and $\bar{\mu}$ is known from experimental measurements[1,2] to be closely proportional to $c-c_F$. Therefore, since both $c^*\{M'(t)\}^2$ and $c^*M'(t)$ vary as $c-c_F$, $M'(t)$ is independent of concentration and c^* varies as $c-c_F$. These are precisely the conditions that permit the introduction of an effective concentration c^* into Eqs. (3) and (5), and our model is, therefore, self-consistent.

The actual values of c^* and $M'(t)$, calculated from both $\bar{\mu}$ and the extrapolated forward cross sections, are listed in Table II, together with the value of $\bar{\mu}$ (obtained by interpolation from experimental data).[1,2] For the 6.3%-nickel specimen, saturation effects prevent a meaningful analysis. Values of $M'(i)$ and $M'(h)$, listed in Table II, were derived from c^* and the fitted quantities A and B. Within experimental error, the nickel $3d$ moment $M'(i)$ and the total moment per impurity $M'(t)$ are independent of concentration with values of $0.9\mu_B$ and $4.6\mu_B$, respectively. The value for the nickel moment may be compared with values obtained by Cable et al.[11] from neutron-scattering measurements on more concentrated Pd-Ni alloys. They find that the nickel $3d$ moment increases steadily as the palladium concentration increases to a value of about $1.2\mu_B$ in a 7.7%-nickel alloy. It appears, therefore, that the nickel moment decreases slightly with further palladium additions.

The values of c^* listed in Table II are equal, within error limits, to $c-c_F$. Thus, the dilute alloys behave as if only those nickel atoms in excess of the critical concentration are effective in creating aligned polarization distributions. This behavior can only be accounted for by a detailed model for the ferromagnetism of the Pd(Ni) system. Perhaps each nickel atom that is relatively well separated from all other nickel atoms, because of the random nature of the alloy, is not ferromagnetically aligned and does not produce an aligned polarization distribution. Alternatively, it may be that the polarization distributions can only be produced by the interaction of nearby nickel atoms, so that the distributions are centered on near-neighbor groups of nickel atoms, rather than on single atoms. In this case, c^* would represent the concentration of near-neighbor groups, and $M'(i)$ is the average magnetic moment of a group, but the analysis given above would not apply in detail because the form factor $f_i(\vec{\kappa})$ for a group of nickel atoms would have structure in addition to that of the atomic $3d$ form factor. The calculated concentration of nickel atoms that have one or more nickel near neighbors is very close to the value of c^* for the 3.0%- and 3.4%-nickel alloys. Although

Table II. Analysis of the results in Table I in terms of a model with an effective concentration c^* of the aligned polarization distributions. c is the chemical concentration of nickel atoms, $\bar{\mu}$ is the moment per atom obtained from magnetization measurements, and $M'(t)$, $M'(i)$, and $M'(h)$ are the derived values of the total moment per aligned polarization distribution, the moment per nickel atom, and the matrix moment per polarization distribution, respectively.

c (at.%)	$\bar{\mu}$ (μ_B)	c^* (%)	$M'(t)$	$M'(i)$	$M'(h)$
			(μ_B/aligned polarization cloud)		
3.0	0.042	0.9	4.6	0.87	3.7
3.4	0.058	1.1	5.1	0.91	4.2
4.7	0.107	2.6	4.1	0.93	3.2
Representative error		±0.5	±1.6	±0.18	±1.4

this observation should not be given too much weight, it does suggest that the magnitudes obtained for c^* are physically reasonable.

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INTERACTION EFFECTS ON THE APPEARANCE OF A MAGNETIC MOMENT ON Co, THROUGH NUCLEAR SPECIFIC-HEAT MEASUREMENTS ON Au:Co ALLOYS*

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The specific heat of Au:Co alloys down to 0.02 K is reported. The nuclear term (AT^{-2}) is due to the magnetic Co atoms which are found to be those included in groups of three and more neighbors. The low-temperature linear term (γT) is the sum of the contributions of the magnetic Co groups, nonmagnetic pairs, and isolated atoms. We estimate fluctuation temperatures of 50 K for the pairs and 700 K for the isolated atoms.

The available data on the Au:Co system show that at low concentrations the alloys are nonmagnetic while phenomena which are generally considered as characteristic of the existence of a localized magnetic moment on the impurity are found at higher concentrations of Co.

Firstly, the resistivity shows a flat $\rho(T)$ behavior for the low concentrations, but a large minimum is observed for concentrations over 0.1%.[1]

Secondly, the magnetization[2] is of Pauli type and remains small compared with alloys of the Cu:Mn type for the low concentrations, but for concentrations over 1% a remanent magnetization and a susceptibility maximum are observed.

Thirdly, above 1 K, specific-heat measurements[3] show an electronic term, concentration dependent, for concentrations below 3%, but for increasing concentrations a tendency towards a concentration-independent behavior is observed. Similar remarks can be made for the Cu:Co[4] system. In the early classification of Blandin and Friedel this has been considered a critical case, i.e., one for which the criterion for magnetism is almost realized: $U\rho(E_F)-1\sim 0$.[5] [$\rho(E)$ is the density of states in the unsplit virtual bound state for one spin direction.]

The theory of localized spin fluctuations[6] has given rise to the notion of a fluctuation temperature[7] T_{SF} $[1/KT_{SF}=\Pi\rho(E_F)/(1-U\rho E_F)]$ which would separate a nonmagnetic state (well below T_{SF}) and a state where the impurity would exhibit all the properties of a magnetic impurity.[8] Caroli has shown $\rho(E_F)$ to be sensitive to the interactions with other impurities.[9] Thus the fluctuation temperature should depend on the interaction; Lederer has shown that the susceptibility is different for an isolated impurity and an interacting pair.[10] Such an analysis is particularly convenient in the case of Co [where $1-U\rho(E_F)\sim 0$] since a moderate interaction may be sufficient to make T_{SF} change by several orders of magnitude. Recently Tournier and Blandin[4] interpreted magnetic results on the Cu:Co system with this argument, attributing a lower fluctuation temperature to the groups of two atoms than