Effect of high magnetic fields on the heat capacity of strongly Pauli-paramagnetic Pd-Ni alloys

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The low-temperature [(1.3—20.0)-K] heat capacity of strongly Pauli-paramagnetic Pd-Ni alloys containing 0.47 and 0.97 at.% Ni was measured in magnetic fields up to 10 T. The electronic specific-heat constant becomes smaller with increasing fields (12% or 13% at 9.98 T). This is probably due to the depression of the spin-fluctuation enhancement of heat capacity by the high magnetic fields and is in accord with the recent theoretical predictions. The coefficient β of the T^3 term in the heat capacity becomes larger with increasing fields and at $H \gtrsim 5.39$ T it reaches almost the same value as that for alloys containing more than ~ 5 at.% Ni. Two possible mechanisms have been proposed to account for the increase in β: (1) The increase is due to the magnetic quenching of localized spin fluctuations in the vicinity of the nickel atoms, or (2) the increase is due to a magnetic contribution to the heat capacity which results from an induced magnetic moment on the nickel atoms by the applied magnetic field. Additional experiments are needed to determine which mechanism is the correct one.

I. INTRODUCTION

The recent discovery of the quenching of spin fluctuations in highly enhanced paramagnetic materials, i.e., $LuCo_2$,[1] Pd,[2] Sc,[3] and $CeSn_3$ (Ref. 4) suggests that a similar effect might be observed in palladium alloys containing small amounts of nickel (~ 1 at.%), since this alloy system has been considered as an ideal system in which to test spin-fluctuation theories of dilute alloys.[5] Palladium is well known as an exchange-enhanced metal—the Stoner factor S has been estimated to vary from 8 to 50; the latest estimate for Pd being $S_0 \simeq 10$.[6] If one adds about 2.25 at.% Ni, the system becomes ferromagnetic,[7] i.e., $S \rightarrow \infty$. Therefore, for compositions between 0 and 2.25 at.% Ni, S will have values ranging from approximately 10 to ∞ (assuming a uniform enhancement model). Kouvel and co-workers[8,9] have proposed a cluster model for this system in which, at concentrations approaching the critical concentration, the clusters interact to cause the system to go ferromagnetic. Low-temperature heat-capacity measurements of Pd-Ni alloys made by Schindler and Mackliet[10] and by Chouteau *et al.*[11] showed a striking increase in the electronic specific-heat constant γ as small amounts of Ni are alloyed with Pd, exhibiting a maximum near the critical concentration (2.25 at.% Ni).

While this effect seems closely related to the mass-enhancement effect in a uniform system with large exchange enhancement,[12–14] it has been pointed out by Lederer and Mills[15] that exchange enhancement in the vicinity of the Ni atoms in the alloy will lead to important changes in the details of the mass-enhancement mechanism. Namely, they have introduced the notion of local enhancement in dilute alloys, i.e., the intra-atomic Coulomb interaction is increased in the vicinity of a solute atom. This model yields a compositional dependence of the low-temperature electrical resistivity of Pd-Ni alloys which is in better agreement with the experimental results than that obtained by the uniform enhancement model. However, since the Lederer and Mills model is a dilute impurity model, the model does not apply for compositions of Ni greater than about 1%.

Chouteau *et al.*[16] have also found that the concentration dependence of the coefficient of the T^3 term β in the normal heat-capacity expression $C = \gamma T + \beta T^3$ for the Pd-Ni alloys decreases linearly with increasing Ni concentrations and reaches $\sim \frac{1}{2}$ of the value for a "pure" Pd metal at the critical concentration around 2.25 at.% Ni. At higher nickel concentration, β increases and at 5 at.% Ni, β has regained the pure Pd value ($\beta \approx 0.15$ mJ/g-at.K^4). However, the Θ_D corresponding to this β value for their pure Pd does not agree with the accepted Θ_D value for Pd; this point will be discussed later. They have interpreted this concentration dependence of β to be due to two sources.[16] One contribution is associated with the mass defect of the impurity which results in a change in the elastic coupling. The other contribution is associated with the local exchange-enhancement increase occurring in the vicinity of the Ni atoms. They have shown that the former contribution is small compared to the latter and have estimated a value of 20 K for the local spin-fluctuation temperature $T_{s,\mathrm{loc}}$, and 400 K for $T_{s,0}$, the spin-fluctuation temperature for pure Pd metal. However, recent heat-capacity measurements[2] as a function of magnetic field indicate that the latter number is much too large and should be of the order of 10 K.

The low value of $T_{s,\mathrm{loc}}$ in Pd-Ni alloys suggests that physical properties which have a local paramagnon contribution may be sensitive to an applied magnetic field. Actually, a strong field dependence of the electrical resistivity at low temperatures has been observed in the dilute paramagnetic Pd-Ni alloys by Schindler and LaRoy[17] and others.[18] They have measured the electrical resistivity of

alloys containing 0—2.0 at. % Ni at temperatures between 1.5 and 4.2 K and in the magnetic fields of up to 9.3 T, and have found that the coefficient of a term proportional to T^2 decreases with increasing fields, the tendency being stronger with increasing Ni concentrations.

On the other hand, more recent measurements[8,9] of the magnetic susceptibility of Pd-Ni alloys with *concentrations greater than 1.3 at. % Ni* indicate that in addition to the exchange enhancements in the vicinity of the single Ni impurity atoms, statistical concentration fluctuations result in the appearance of nearest-neighbor Ni pairs and groups of three or more Ni atoms (i.e., Ni triads). The Ni atom pairs simply make a large contribution to the relatively temperature-independent (exchange-enhanced) component of the susceptibility while the Ni triads appear to exhibit a stable giant moment of $18\mu_B$ and a spin of 2. The heat-capacity contributions for such a system of triads would give rise to an upswing in a C/T vs T^2 plot at temperatures less than 2 K in a magnetic field greater than 3 T, while at lower fields no anomaly would be seen. This behavior is clearly not the same as observed in the recent measurements of heat capacity as a function of magnetic field for the strong Pauli paramagnets Sc (Ref. 3) and $CeSn_3$ (Ref. 4) which have shown, in addition to the quenching of spin fluctuations by the field, the presence of an additional T^3 heat-capacity contribution due to the magnetic moments induced by the applied magnetic field.

In the present work, heat-capacity measurements of the Pd-Ni system were made on samples containing less than 1 at. % Ni. Since the concentration of isolated Ni atoms goes as c, that of pairs as c^2, and of triads as c^3, it is presumed that the spin-fluctuation effects would be dominant for these low concentrations. However, it is felt that if Ni triads are present, measurements made in magnetic fields of up to 10 T and at temperatures (1.3—20 K) would exhibit the upturn in C/T vs T^2 as noted previously.

II. EXPERIMENTAL

The cylindrical alloy specimens, roughly 2.5 cm long by 2.5 cm diam, were prepared by induction melting 99.999% pure Pd and Ni. The specimens were melted under a purified argon atmosphere in quartz crucibles. Each ingot was surface ground on both ends and carefully annealed at 1200 °C for 20 h. The Pd-Ni alloy specimens (~8 g) for the heat-capacity measurements in magnetic fields were cut from these ingots, which were the same as those used in the zero-field low-temperature heat-capacity measurements.[10] Colorimetrical chemical analyses of the final ingots indicated that less than 8 ppm at. % Fe and 5 ppm at. % Co (the lower limits of detection) were present in both Pd-Ni alloy samples.

The low-temperature calorimeter used in this investigation is an isolation heat-pulse type with a mechanical heat switch. The temperature was measured by using a germanium resistance thermometer which had been calibrated at magnetic fields of 0, 2.50, 5.39, 7.62, and 9.98 T.[19] The heat capacity of the 1965 Calorimetry Conference standard copper sample was measured to serve as a check of the apparatus and experimental technique. The results obtained on our copper standard sample were in agreement within ±1% at 0 T and ±2% at the four nonzero magnetic fields with the previous zero-field data.[20]

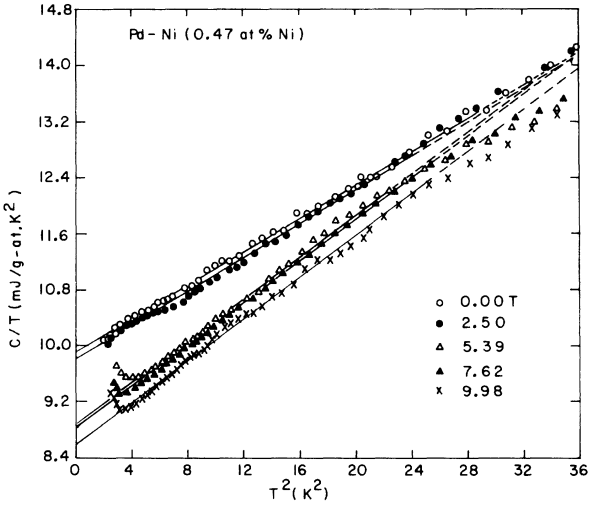

FIG. 1. Heat-capacity data for Pd—0.47 at. % Ni in the magnetic fields of 0, 2.50, 5.39, 7.62, and 9.98 T. The solid lines are the results of a least-squares fitting of the data for each field to the equation $C/T=\gamma+\beta T^2$.

III. RESULTS

The heat-capacity measurements were made from 1.3 to 20.0 K on two Pd-Ni alloys containing 0.47 and 0.97 at. % Ni at magnetic fields of 0, 2.50, 5.39, 7.62, and 9.98 T. Figures 1 and 2 show the results of our measurements below 6 K for the Pd-Ni alloy containing 0.47 and 0.97 at. % Ni, respectively, while Figs. 3 and 4 present the zero field and 9.98-T data up to 20 K. The C/T vs T^2 curves in zero field for both specimens are almost the same as the previous results by Schindler and Mackliet[10] and by

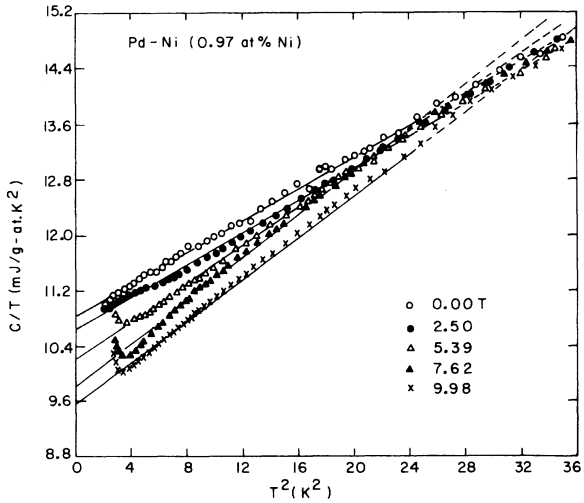

FIG. 2. Heat-capacity data for Pd—0.97 at. % Ni in the magnetic fields of 0, 2.50, 5.39, 7.62, and 9.98 T. The solid lines are the results of a least-squares fitting of the data for each field to the equation $C/T=\gamma+\beta T^2$.

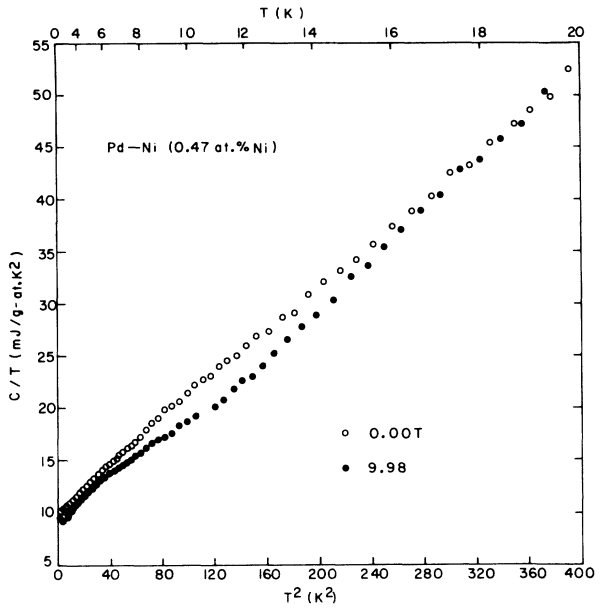

FIG. 3. Heat capacity of the Pd-Ni alloy containing 0.47 at. % Ni from 1.3 to 20.0 K at 0 and 9.98 T.

Chouteau *et al.*[11] With increasing magnetic fields, however, one can distinctly see that the C/T vs T^2 curves fall and their slopes become steeper.

As can be seen, all C/T curves for the 0.47 and 0.97 at. % Pd-Ni alloys are linear, and there is no evidence for a $T^3 \ln T$ term in our data, except possibly for the slight upturn noted in 5.39-, 7.62-, and 9.98-T field data. The absence of an upturn at $H=0$ and 2.50 T would tend to rule out the existence of a $T^3 \ln T$ contribution to the heat capacity which is in agreement with the zero-field heat-capacity measurements previously reported.[10,11] A reasonable explanation for the upturn found for $H > 2.5$ T is

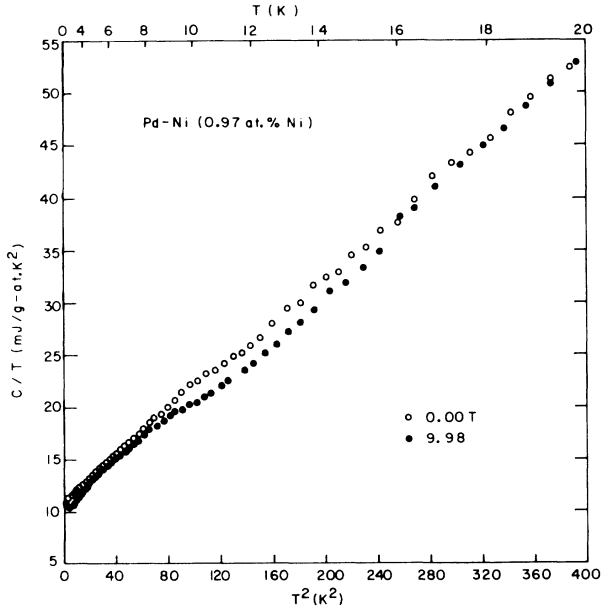

FIG. 4. Heat-capacity data of the Pd-Ni alloy containing 0.97 at. % Ni from 1.3 to 20.0 K at 0 and 9.98 T.

TABLE I. The results of a least-squares fit of the heat-capacity data of the Pd-Ni alloys for each of the five magnetic fields to the equation $C/T=\gamma+\beta T^2$.

at. % Ni	H (T)	γ (mJ/g-at. K^2)	β (mJ/g-at. K^4)	Effective Θ_D (K)
0.47	0.00	9.90	0.118	254
	2.50	9.79	0.123	251
	5.39	8.87	0.149	235
	7.62	8.80	0.150	235
	9.98	8.57	0.150	235
0.97	0.00	10.85	0.115	257
	2.50	10.66	0.116	256
	5.39	10.00	0.145	238
	7.62	9.84	0.150	235
	9.98	9.56	0.151	235

that this increase is due to the superparamagnetic behavior of nickel triads[8,9] or of dilute magnetic impurities such as iron. Since the chemical-analysis data indicated quite small magnetic impurities, it was unlikely to affect other data reported here. Consequently, the slight upturn at high fields was ignored in the data analysis.

The electronic specific-heat constant γ and the apparent Debye temperature at 0 K, Θ_D, were calculated for each field between 1.3 and 5.0 K by a least-squares fit of the data to the equation

$$C/T=\gamma+\beta T^2 . \quad (1)$$

The γ, β, and apparent Θ_D values are presented in Table I and the field dependence of the first two quantities are plotted in Fig. 5. Contrary to the data found for pure Pd[2], both γ and β are found to be field dependent. As the magnetic field increases, the γ values for both samples decrease slowly, fall more rapidly between 2.5 and 5.39 T, and then continue to fall slowly at the highest fields. A similar but opposite effect is found for β. The values of β for both samples initially increase slowly with magnetic field, then increase more rapidly between 2.5 and 5.39 T, and become almost constant above 7.62 T.

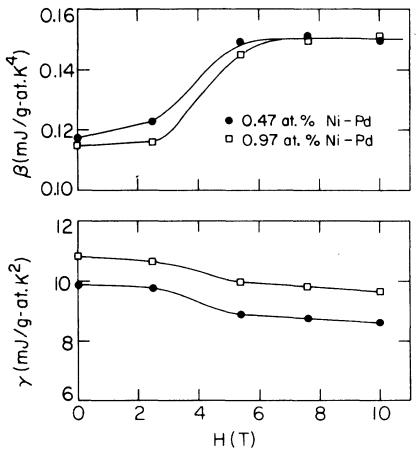

FIG. 5. Electronic specific-heat constant γ and the coefficient β of the T^3 term for the Pd-Ni alloys containing 0.47 and 0.97 at. % Ni as a function of the magnetic field to 9.98 T.

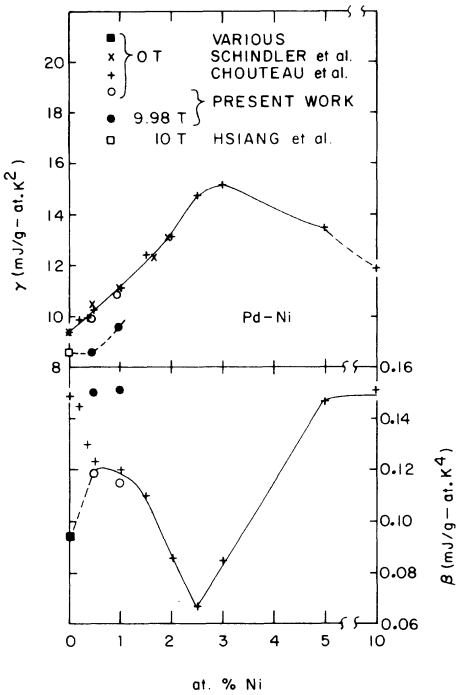

FIG. 6. Comparison of our low-temperature heat-capacity results at 0 and 9.98 T with the previous data by Schindler and Mackliet (Ref. 10) and by Chouteau *et al.* (Refs. 11 and 16). The β value for pure Pd is based on both heat-capacity measurements on high-purity Pd-metal (Refs. 2 and 21) and elastic constant measurements (Ref. 22) (β was calculated from the Θ_D derived from the c_{ij} values). The β values for Pd and the two lowest Ni containing Pd alloys reported by Chouteau *et al.* are in error, probably because of the presence of 70 ppm (probably by weight) of Fe in their Pd.

Figure 6 shows the value of γ and β as a function of composition in zero field and at $H=9.98$ T for pure Pd (Ref. 2) and for the Pd-Ni alloys containing 0.49 and 0.97 at. % Ni, along with the zero-field results of Schindler and Mackliet[10] and of Chouteau *et al.*[9,16] Our results in zero field are in good agreement with these previous data. It should be noted that the value of Θ_D for pure Pd was found to be field independent. The values found for the field dependence of γ are consistent with that found for pure Pd; a substantial decrease was observed for pure Pd,[2] and even larger decreases have been found by us for the two Pd-Ni alloys. The rapid change in β with alloying (a -7% change in apparent Θ_D) may seem to be unusual, but similar changes have been observed in alloys involving nonmagnetic solutes, e.g., changes in Θ_D of -4% and $+6\%$ have been found for Mg and Zr, respectively, dissolved in Sc.[23] Furthermore, we cannot rule out the possibility that there is a magnetic effect which accounts for the increase of Θ_D when Ni is added to Pd. This will be discussed in more detail later. Furthermore, it should be noted that the β values at 9.98 T of both alloys are nearly equal to those of the concentration magnetic alloys with concentrations of Ni greater than 5 at. %.

The temperature dependence of the heat capacity of both samples for temperatures up to 20 K at both zero field and at $H=9.98$ T are shown in Figs. 3 and 4. Plotted as C/T vs T^2, the heat capacity of each sample measured in a magnetic field lies below the zero-field data. This negative shift increases as T increases, becoming a maximum at T approximately 10—12 K and vanishes (the heat capacities become field independent) above 16 K.

IV. DISCUSSION

In this section the magnetic field dependence of the low-temperature heat capacity of the Pd-Ni alloys is discussed in connection with a model based on spin-fluctuation suppression and one based on induced magnetic moment effects. In neither case has the theory been developed to fit the case of the field dependence of the specific heat in Pd-Ni alloys, but reasonable extensions to the available theory can be made and compared with experimental results.

A. Quenching of spin fluctuations by magnetic fields

As has been seen in Fig. 5, both γ and β exhibit a strong dependence on magnetic field. The decrease in γ for these alloys as well as for pure Pd is unusually strong. In fact, $\Delta\gamma$ for the alloys are greater than twice that found for pure Pd. Since it has been found that β for pure Pd is field independent, it is a reasonable assumption that the large field dependence of γ and β for the Pd-Ni alloys must be in some way related to the fact that one is dealing with an alloy system.

A theory for the field dependence of the specific heat based on spin-fluctuation effects has been treated only for the case of uniform enhancement, i.e., the Stoner enhancement factor S is the same at every site of the lattice. Obviously this is not true for alloys, but a rough notion of the effect of alloys can be made by presuming that alloying, in this case, Ni with Pd, S will vary from 10, that of pure Pd, to ∞ at the ferromagnetic composition (2.25 at. % Ni). For such a strong Pauli-paramagnetic metal, in the uniform enhancement model, the low-temperature heat capacity, well below T_s, has been theoretically[12,13,24–26] shown to be

$$C=\gamma_0 T[m^*/m+\alpha(T/T_s)^2\ln(T/T_s)+\cdots]+\beta_0 T^3 . \tag{2}$$

Here m^*/m is the zero-temperature many-body mass enhancement, which includes spin-fluctuation and electron-phonon contributions, γ_0 is the electronic—specific-heat constant determined from the band-structure density of states, α is proportional to $S(1-S^{-1})^2$, and $\beta_0 T^3$ is the usual lattice contribution.

Béal-Monod *et al.*,[27] using the Maxwell relation $\partial M/\partial T=\partial S^*/\partial H$ (M is the magnetization and S^* is the entropy), have shown that the shift of the electronic specific-heat constant at 0 K caused by an applied field H,

$$\frac{\delta\gamma}{\gamma(0)}=\frac{\gamma(0)-\gamma(H)}{\gamma(0)}\approx\frac{C(0)-C(H)}{C(0)} ,$$

should be

$$\frac{\delta\gamma}{\gamma(0)}\approx 0.1\left[\frac{S}{\ln S}\right]h^2 , \tag{3}$$

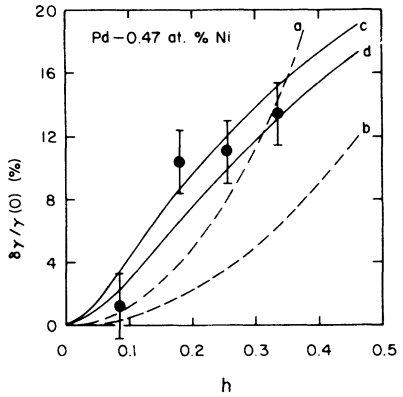

FIG. 7. Shift of the electronic specific-heat constant at 0 K, $\delta\gamma/\gamma(0)=[\gamma(0)-\gamma(H)]/\gamma(0)$, in Pd–0.47 at. % Ni caused by an applied field as a function of the reduced field $h=\mu_B H/k_B T_s$. The theoretical curves are from Béal-Monod *et al.* (Ref. 27) (curve *a*: $S=50$; curve *b*: $S=15.3$) and from Hertel *et al.* (Ref. 28) assuming $S=50$ and $\lambda_{\rm spin}(0)=0.56$ (curve *c*: $a^2=0.5k_F^2$; curve *d*: $a^2=1k_F^2$).

where $h=\mu_B H/k_B T_s$. Assuming a uniform enhancement model, the Stoner exchange enhancement factor S is calculated to be 15.3 for the Pd–0.47 at. % Ni and 23.9 for the Pd–0.97 at. % Ni alloys by using the measured magnetic susceptibilities at 4 K (Ref. 10) and $S_{\rm Pd}=10$.[5] Since the system is more nearly ferromagnetic than pure Pd, a value of $T_s=20$ K was adopted for these dilute Ni-Pd alloys. (This is approximately equal to the local spin-fluctuation temperature for these alloys.) If a smaller value for T_s is used, the discrepancy between the calculated and observed values are even larger (Figs. 7 and 8). The predicted variation of $\partial\gamma/\gamma(0)$ as a function of h is shown in Fig. 7 as curves *a* ($S=50$) and *b* ($S=15.3$) and in Fig. 8 as curves *a* ($S=50$) and *b* ($S=23.9$) along with the experimental results.

On the other hand, Hertel *et al.*[28] have recently made a more detailed mathematical analysis of the influence of the magnetic field on the spin-fluctuation enhancement of the electronic specific heat, again using a uniform enhancement model. They have given the effective mass

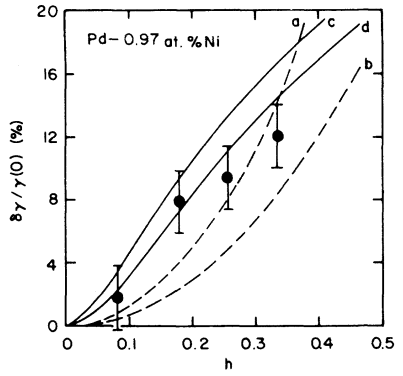

FIG. 8 Shift of the electronic specific-heat constant at 0 K, $\delta\gamma/\gamma(0)=[\gamma(0)-\gamma(H)]/\gamma(0)$, in Pd–0.97 at. % Ni caused by an applied field as a function of the reduced field $h=\mu_B H/k_B T_s$. The theoretical curves are from Béal-Monod *et al.* (Ref. 27) (curve *a*: $S=50$; curve *b*: $S=23.9$) and from Hertel *et al.* (Ref. 28) assuming $S=50$ and $\lambda_{\rm spin}(0)=0.65$ (curve *c*: $a^2=0.5k_F^2$; curve *d*: $a^2=1k_F^2$).

enhancement $\lambda_{\rm spin}(H)/\lambda_{\rm spin}(0)$ as a function of the reduced field $h=\mu_B H/k_B T_s$ for a metal with $S=50$, 10, and 4. We have calculated the magnetic field dependence of $\partial\gamma/\gamma(0)$ from the following equation by using their results for the case of $S=50$:

$$\frac{\delta\gamma}{\gamma(0)}=\frac{\lambda_{\rm spin}(0)}{1+\lambda_{\rm ph}+\lambda_{\rm spin}(0)}\left[1-\frac{\lambda_{\rm spin}(H)}{\lambda_{\rm spin}(0)}\right]. \tag{4}$$

By assuming that the dilute Ni-Pd alloys have the same values of γ_0 and $\lambda_{\rm ph}$ as those for Pd, $\lambda_{\rm ph}=0.20$ (Ref. 29) and $\lambda_{\rm spin}(0)=0.37$ (Ref. 28) for Pd, the $\lambda_{\rm spin}(0)$ values were estimated to be 0.56 for 0.47 at. % Ni and 0.65 for 0.97 at. % Ni alloys from the measured γ values. Figures 7 and 8 also show the analyzed results obtained from the model of Hertel *et al.* for the metals with $S=50$ and the values of potential parameter $a^2=0.5k_F^2$ (curve *c*) and $1k_F^2$ (curve *d*).

The experimental results for the Pd-Ni alloys containing 0.47 and 0.97 at. % Ni (Figs. 7 and 8) are in fair agreement with the *c* and *d* curves of Hertel *et al.* For the model of Béal-Monod *et al.*, the agreement is poor although the experimentally derived parameter of S is used to calculate curve *b*. However, it should be noted that the Béal-Monod model is derived for a uniform system (and not for one in which there are local enhancements due to Ni impurities) and a parabolic band, which is not the case here either.

A more appropriate model for the field dependence of γ and β for dilute Pd-Ni alloys should be one based on a local enhancement model. Such a case for dilute exchange-enhanced alloys, where the dilute solute atoms do not exhibit permanent moments, but tend to drive the system towards the ferromagnetic phase, has been treated by a number of authors.[15,16,24] They have introduced the concept of local enhancement and have considered the consequences of such a local enhancement of a number of properties using a single impurity calculation. Following the procedures of Chouteau *et al.*,[16] the extra specific heat per impurity atom can be written as

$$\frac{\Delta C}{T}\approx\Delta\gamma_0\left[1+\frac{6\pi^2}{5}\frac{S_0(S_0-1)}{\kappa}\left[\frac{T}{T_{s,0}}\right]^2\ln\left[\frac{T}{T_{s,0}}\right]-\frac{4\pi^2}{5}\left[\frac{T}{T_{s,\rm loc}}\right]^2\right], \tag{5}$$

which when added to the specific heat of the solvent yields

$$\frac{C}{T}\approx\gamma_0\left[1+c\frac{\Delta\gamma_0}{\gamma_0}\right]+\beta_0\left\{T^2+c\frac{\Delta\gamma_0}{\beta_0}\left[\frac{6\pi^2}{5}\frac{S_0(S_0-1)}{\kappa}\left[\frac{T}{T_{s,0}}\right]^2\times\ln\left[\frac{T}{T_{s,0}}\right]-\frac{4\pi^2}{5}\left[\frac{T}{T_{s,\rm loc}}\right]^2\right]\right\}, \tag{6}$$

where

$$\kappa=\lim_{\omega\to 0}\frac{\sum_q {\rm Im}\chi_{\rm Pd}(q,\omega)}{\sum_q {\rm Im}\chi_0(q,\omega)}$$

and c is the concentration of the solute.

These results are similar to that of the uniform enhancement calculation, Eq. (2) in that there is an electronic specific-heat term which is linear in temperature plus a $T^3 \ln T$ term both of which are related to enhancement factors which are associated with the uniform matrix, suitably modified because of the presence of the dilute exchange-enhanced impurities and which vary linearly with concentration. In addition, the calculations also yield a $-T^3$ term which is also (necessarily) linear with concentration and depends on exchange enhancement localized around the impurity atoms. (Effects due to the mass defect of the impurity atoms and to the change in the elastic coupling have, however, been omitted.) Chouteau *et al.*[16] have found experimentally that at low temperatures (<3 K) the $T^3 \ln T$ term exhibits a T^3 dependence, mixes in with the $-T^3$ term from the local enhancement, and results in a modified lattice term yielding an apparent Θ_D. The total expression at low temperature and for dilute impurities can then be written

$$\frac{C}{T} \approx \gamma_0 \left[1 + c \frac{\Delta\gamma_0}{\gamma_0} \right] + [\beta_0 + c\Delta\gamma_0(\Delta\beta_1 - \Delta\beta_2)] T^2 , \quad (7)$$

where $\Delta\gamma_0$ can be obtained from the exchange-enhancement model of Mills and Lederer and $\Delta\beta_1$ and $\Delta\beta_2$ are obtained experimentally or from Eq. (6).

As can be seen from a comparison of Eqs. (1), (2), and (7), the experimental electronic specific-heat constant γ and the coefficient of the T^3 term of heat capacity β are, respectively, expressed by the following equations:

$$\gamma = \gamma_0(m^*/m) = \gamma_0(1+\lambda) = \gamma_0 \left[1 + c \frac{\Delta\gamma_0}{\gamma_0} \right] , \quad (8)$$

$$\beta = \beta_0 + c\Delta\gamma_0(\Delta\beta_1 - \Delta\beta_2) . \quad (9)$$

Thus if Eq. (6) is valid the resultant Θ_D value calculated from β is not the true Debye temperature, as we have already observed.

It has further been shown by Engelsberg *et al.*[24] that one can write the leading term in the specific heat as

$$\Delta\gamma \approx \frac{3c\gamma}{2} \left[\frac{3+(S-1)\sigma}{3S} \right] \frac{1}{\chi} \left[\frac{d\chi}{dc} \right]_{c=0} , \quad (10)$$

where σ is a range parameter associated with the range of the polarization surrounding an isolated Ni atom in the Pd lattice, and $(d\chi/dc)_{c=0}$ is the concentration dependence of the magnetic susceptibility evaluated at $c=0$. An estimate for the field dependence of γ can be obtained by estimating the field dependencies of the various parameters in Eq. (10). Since it is unlikely that the magnetic field will modify the range parameter significantly, and since S is the Stoner enhancement factor of pure Pd, the main dependence is that of $(1/\chi)(d\chi/dc)$ and of γ. Experimentally, both γ and $(1/\chi)(d\chi/dc)$ have been found[30] to decrease substantially with applied magnetic field. This would suggest that γ of the alloys would be even more strongly field dependent than that of pure Pd, which is in accord with the experimental results. However, Eq. (10) would also indicate that in the presence of a magnetic field $\Delta\gamma$ should still increase linearly with composition. Clearly this is not in accord with the experimental results, see Fig. 6.

Likewise, the variation of β with magnetic field can, with only modest success, be interpreted within the framework of the local spin-fluctuation model. Recall that the linear variation of β with concentration (up to ~ 2 at.% Ni) has been interpreted by Chouteau *et al.* as arising from the $c\Delta\gamma_0(\Delta\beta_1 - \Delta\beta_2)$ term of Eq. (7) mixing in with the "normal" phonon contribution to the T^3 term. $\Delta\beta_1$ arises from the uniform exchange enhancement of the Pd lattice and $\Delta\beta_2$ is related to local enhancement effects from the dilute Ni atoms. Since Hsiang *et al.*[2] found that β remained constant as the magnetic field was increased from 0 to 11 T, we would expect $\Delta\beta_1$ to be essentially field independent, while $\Delta\beta_2$ might be quenched by a strong magnetic field. However, since $\Delta\beta_2$ is proportional to $1/T_{s,\mathrm{loc}}$ [see Eq. (5)] and $T_{s,\mathrm{loc}} \approx 20$ K[16] (later experiments[31] appear to indicate that this number should be associated with Ni clusters), the effective field is ≈ 30 T (assuming $s = \frac{1}{2}$), nearly 6 times larger than that observed. Thus it is unlikely the $\Delta\beta_2$ is affected by the applied field. But as indicated in Eqs. (6), (7), and (9), the field dependence of β depends upon the product $\Delta\gamma_0(\Delta\beta_1 - \Delta\beta_2)$, and $\Delta\gamma_0$ is known to decrease with increasing field [Eq. (8) and Fig. 5]. If the term $\Delta\beta_1 - \Delta\beta_2$ is negative, then β should be expected to increase [Eq. (9)]. As seen from Eqs. (5) and (6), the first term $\Delta\beta_1$ is negative by virtue of $\ln(T/T_{s,0})$, since $T_{s,0}$ is ~ 400 K, and since $\Delta\beta_2$ is a positive quantity the expression $\Delta\beta_1 - \Delta\beta_2$ is always negative. Thus it is possible that the local enhancement model might explain the observed behavior.

Theoretical studies of spin fluctuations predict the anomalous enhancement of the electronic specific heat due to the spin fluctuations at low temperatures (that is, the mass enhancement), the appearance of the $T^3 \ln(T/T_s)$ term[12,13,25] and the spin-fluctuation contribution to the apparent β may be quenched by high magnetic fields.[25,27,28] Brinkman and Engelsberg[25] have explained that high magnetic fields of the order of the characteristic spin-fluctuation temperature are required to quench the spin-fluctuation enhancement to the heat capacity. Making use of the relationship $\mu_B H_{\mathrm{eff}} = k_B T_s$, which assumes $s = \frac{1}{2}$ and where μ_B is the Bohr magneton and k_B is the Boltzmann's constant, and the T_s value given by Chouteau *et al.*[16] (20 K), we find that the field required to quench spin fluctuations, H_{eff}, is 30 T.

Recently Béal-Monod and Daniel[32] pointed out that the correct expression is $\mu_B H_{\mathrm{eff}} = S^{-1/2} k_B T_s$, and this results in H_{eff} values of 7.6 and 6.1 T for the 0.47 and 0.97 at.% Ni-Pd alloys, respectively. These values are consistent with our results shown in Fig. 5.

B. Induced magnetic moments

As observed earlier, the field dependence of β is quite different from that found for $LuCo_2$ (Ref. 1) and pure Pd (Ref. 2), both of which exhibit a field-independent β. On the other hand, both $CeSn_3$ (Ref. 4) and Sc (Ref. 3) were found to have β values which depended upon the magnetic field in the same manner as shown in Fig. 5 for the Ni-Pd alloys. For the $CeSn_3$ and Sc the zero-field heat-capacity β values yield a Θ_D value which was in excellent agreement with the corresponding Θ_D calculated from inelastic neutron scattering data. Furthermore, in the case of $CeSn_3$, neutron scattering experiments at high magnetic

fields showed the presence of an induced magnetic moment on the Ce atoms caused by an applied field of 4 T.[33] Ikeda and Gschneidner[4] concluded that this induced magnetic moment gives rise to a T^3 contribution to the heat capacity at high magnetic fields (>1 T), i.e., β increases as a function of magnetic field. One also might presume that a similar effect could occur in the Pd-Ni alloys.

In order to test whether a similar behavior to that found for $CeSn_3$ and Sc was exhibited in the Pd-Ni alloys, an attempt was made to estimate the excess magnetic heat capacity C_M and to determine its temperature dependence. The observed heat capacity C_T was partitioned into the following contributions:

$$C_T = C_E + C_L + C_M f(H) = C_E + \beta_0 T^3 + C_M f(H) , \tag{11}$$

where C_E and C_L are, respectively, the electronic and lattice contributions to the heat capacity. The C_E term (which is equal to γT) is obtained from the measured γ value as determined at each field. The lattice contribution is derived from the β value at zero magnetic field. The assumption here is that the zero-field β value corresponds to the true Θ_D value and that it is independent of the magnetic field. This is reasonable since the Debye temperatures for the two Ni-Pd alloys, as calculated from the zero-field values, are in fairly good agreement with the Debye temperature of pure Pd.[2,21,22] In all cases, for both alloys at magnetic fields of 5.39, 7.62, and 9.98 T, C_M is found to vary roughly as T^3 from ~ 2 to ~ 5 K (e.g., see Fig. 9), reaching a peak between 5 and 7 and then dropping to zero and going negative between 7 and 10 K, depending upon the Ni content; see Table II.

Following this logic, the coefficient of the T^3 term of the heat capacity (β) is assumed to be composed of two contributions, a lattice term (β_0) and a magnetic term (β_M). At zero field, $\beta_M = 0$ and $\beta(H=0) = \beta_0$. Since β_0 should be independent of the applied field, subtracting β_0 from the observed β at fields of 5.39, 7.62, and 9.98 should give β_M. The reasonable agreement of the β_M value calculated in this manner with the variation of C_M as a function of T^3 is shown in Fig. 9.

An estimate of the entropy S_M associated with this excess heat capacity C_M can be made by integrating $\int (C_M/T) dT$. However, the value of C_M obtained by the procedures described above goes through zero at $T = 7$ K and is negative for $T > 7$ K, indicating a breakdown of the approximations employed. In particular, the assumption that $C_L = \beta_0 T^3$ is well known to break down for $T > \theta/50$. Since Θ_D for Pd is of the order of 275 K, we should expect a breakdown in the approximation at $T > 6$ K. Nonetheless, a rough estimate of S_M for the two samples can be obtained (see Table II). The error limits for S_M based on the three determinations of S_M (one at each field) is $\sim 17\%$ for each alloy, which is reasonable because of the approximations used to calculate S_M, and that two large numbers are subtracted from one another to give S_M.

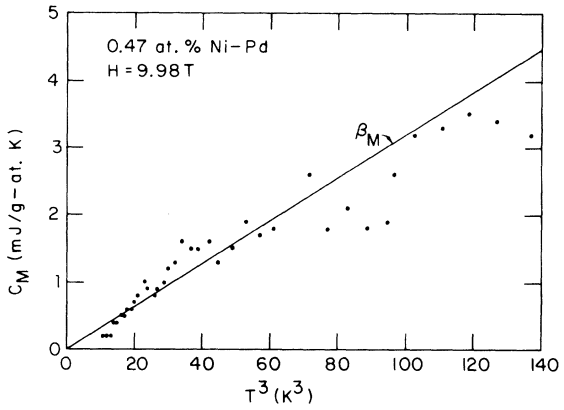

FIG. 9. Plot of the magnetic contribution to the heat capacity (C_M) vs T^3. The coefficient of the magnetic contribution to the heat capacity (β_M), i.e., the slope, was calculated from the experimental β value at $H = 9.98$ T and the zero-field β value (see text).

A theoretical estimate for the excess entropy can be made using a model employed earlier by Gillespie and Schindler[34] for $(Pd\text{-}Rh)_{1-x}Ni_x$ alloys. They found that the magnetic entropy for a system of interacting Ni atoms forming only Ni pairs is

$$S_M = nc^2(1-c)^{n-1} R \ln(2s+1) , \tag{12}$$

where $n+1$ is the number of lattice sites in a sphere containing only two Ni atoms which interact only with each other forming pairs, and c is the concentration. The best agreement between the experimental S_M values (Table II) and those calculated from Eq. (12) was obtained by using values of $n = 12$ and $s = \frac{1}{2}$, which give $S_M = 1.5$ and 5.8 mJ/g-at. K for the 0.47 and 0.97 at. % alloys, respectively.

The main difficulty with this model is that S_M should increase by a factor of 4 when the concentration is doubled, i.e., $\Delta S_M \propto \Delta c^2$, regardless of the values of n and s, while experimentally, S_M only doubles, i.e., $\Delta S_M \propto \Delta c$. This suggests that the magnetic field induces a moment,

TABLE II. Magnetic contribution to the heat capacity.

Alloy (at. % Ni)	Property	Magnetic field (T) 5.39	7.62	9.98	Avg.
0.47	T_{peak} (K)	5.2	5.5	5.6	5.3±0.3
	C_M^{max} (mJ/g-at. K)	3.5	4.0	3.7	3.7±0.3
	β_M (mJ/g-at. K^4)	0.031	0.032	0.032	0.032
	S_M^{expt} (mJ/g-at. K)	2.03	2.68	2.12	2.3±0.4
0.97	T_{peak} (K)	6.8	5.7	5.9	6.2±0.6
	C_M^{max} (mJ/g-at. K)	5.1	5.1	5.8	5.3±0.5
	β_M (mJ/g-at. K^4)	0.030	0.035	0.036	0.034
	S_M^{expt} (mJ/g-at. K)	4.91	3.59	4.46	4.3±0.7

not only on Ni atom pairs (and perhaps triads), but also on isolated noninteracting Ni atoms. The magnetic entropy in this case is given by

$$S_M = cf_d R \ln(2s+1) , \quad (13)$$

where f_d is the number of unpaired d electrons associated with the Ni atoms and spin fluctuations, and c is the total Ni concentration. Assuming that $s=\frac{1}{2}$ and that f_d is the same order of magnitude as that of other spin-fluctuation systems, i.e., $CeSn_3$,[4] Sc,[3] Sc_3In (Ref. 35) (0.001 to 0.01) good agreement can be obtained: for $f_d=0.08$, $S_M=2.2$ and 4.5 mJ/g-at. K for the 0.47 and 0.97 at. % Ni-Pd alloys, respectively. The important thing here is that the entropy change with alloying is proportional to the concentration, as is observed experimentally.

Two possible models have been proposed to explain the increase in β with increasing magnetic field, but unfortunately the present experimental data do not permit one to decide which model is the most likely to be the correct one, i.e., the quenching of localized spin fluctuations or the inducing of a magnetic moment. Accurate susceptibility measurements on these dilute Pd-Ni alloys, such as made by Gillespie and Schindler for Pd–($Rh_{1-x}Ni_x$) alloys[34] would be helpful. But more meaningful information would be realized by neutron scattering studies of single crystals of Pd doped with Ni at $H=0$ and ~ 5 T, where an induced magnetic moment on the Ni sites could be readily and unambiguously determined, as in the cases of $LuCo_2$,[36] $CeSn_3$,[33] and UAl_2.[37]

C. Clustering versus spin fluctuations

At first glance one might believe that the observed effects in the magnetic field dependence of the heat capacity is due to the presence of Ni clusters. Although we cannot rule out that Ni atom clusters exist, the upturn in the heat capacity at $H>5$ T (Figs. 1 and 2) suggests that some Ni clusters may exist, but other magnetic impurities in our alloys such as Fe (<8 ppm at. %) and/or Co(<5 ppm at. %) could also account for such a behavior. It is also conceivable that the increase in β with increasing magnetic field might be due to Ni clusters, however, the mechanism which leads to a T^3 dependence is not evident.

Nickel atom clusters, however, in no way can explain the $\sim 12\%$ decrease in γ with increasing field (Fig. 5), nor why the zero field and 10-T heat capacity are the same above 16 K (Figs. 3 and 4). This behavior follows from spin-fluctuation theory, where the application of a field quenches the spin-enhancement term and thus lowers γ, and at high temperatures (>12 K) the enhancement is suppressed because of the renormalization of the spin fluctuations.[38]

Examination of Figs. 3 and 4 clearly shows that the reduction in γ has a dominant role over the increase in β in determining the total heat capacity at high fields. As noted in the preceding section, C_M reaches a maximum between 5 and 7 K and then drops to zero between 7 and 10 depending upon the nickel content and the applied field. This decrease is due to the thermal energy destroying the alignment of the magnetic moments, and thus B_M also drops to zero in this same temperature interval. This is quite evident in Figs. 3 and 4 as the slope for the 10-T data decreases from ~ 6 to ~ 11 K (36 and 120 in units of T^2 given in the figures). Thus even if the increase in β were due to Ni atom clusters, the influence of spin fluctuations on the heat capacity is still larger. But since spin fluctuations can also account for the increase in β, the magnetic field dependence of the heat capacity of Pd-Ni alloys could be entirely due to spin fluctuations. Until some unequivocal experimental evidence is obtained to show that clustering does contribute to the magnetic and electrical behavior of low concentration (<1 at. % Ni) Pd-Ni alloys, the authors believe that spin fluctuations describe these Pd-rich materials.

V. CONCLUSION

The present work shows that the quenching of the spin-fluctuation enhancement of electronic specific heat in the strongly Pauli-paramagnetic Pd-Ni alloys begins at an applied magnetic field of 4 T. Furthermore, the coefficient to the T^3 term of the heat capacity was also found to exhibit a field dependence similar to that found in $CeSn_3$ (Ref. 4) and Sc.[3] Two possible mechanisms have been proposed to account for the increase in β: (1) the increase is due to a magnetic contribution to the heat capacity which results from an induced magnetic moment on the nickel atoms by the applied magnetic field, or (2) the increase arises from the magnetic quenching of localized spin fluctuations in the vicinity of the nickel atoms. Additional experiments are needed to determine which mechanism is the most plausible one.

Note added in Proof. Recently Roeland *et al.*[39] measured two de Haas–van Alphen (DHvA) orbits in 0.35 and 0.66 at. % Ni-Pd alloys and found a field dependence (up to 40 T) for the Stoner enhancement. These results, although not directly comparable to our heat-capacity results because the DHvA measurements only sampled a small part of the Fermi surface, are consistent with our observations of an $\sim 12\%$ depression of γ by an applied field of 10 T for Pd alloys of comparable Ni concentrations.

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