MAGNETOSTRICTION AND THERMAL EXPANSION OF Pd AND PARAMAGNETIC Pd:Ni ALLOYS

E. Fawcett, E. Bucher, W. F. Brinkman, and J. P. Maita
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 6 August 1968)

The magnetostriction of Pd:Ni alloys shows that the volume derivative of the localized exchange enhancement is large and positive in contrast to the corresponding parameter in Pd. The low-temperature thermal expansion has a logarithmic singluarity near the critical concentration and shows an anomaly in its temperature dependence like that predicted theoretically.

As small amounts of Ni are alloyed into Pd, the low-temperature electronic specific heat increases rapidly[1,2] as does the magnetic susceptibility. This mass enhancement associated with exchange enhancement was predicted for uniform systems,[3-5] but Lederer and Mills[6] pointed out that a model in which the exchange enhancement is localized on the Ni atoms is more physically reasonable. The calculation of Engelsberg, Brinkman, and Doniach[7] for such a model showed that the mass has a logarithmic singularity near the critical concentration for ferromagnetism. They also found that the localized-exchange-enhancement model, like the uniform-enhancement model,[4] contains a term in the low-temperature specific heat of the form $T^3 \ln T$. Fulde and Luther[8] calculated the effects of impurity scattering and concluded that the $T^3 \ln T$ term is likely to be suppressed in disordered alloys. Brinkman and Engelsberg[9] pointed out that the spin-independent impurity scattering replaces the $T^3 \ln T$ behavior of the specific heat C_v by a term having $T^{3/2}$ dependence, which is more singular at zero temperature in the usual plot of C_v/T vs T^2.

To explore this problem we measured the thermal expansion of several paramagnetic Pd:Ni alloys. The thermal expansion divided by the compressibility is the volume derivative of the entropy and should exhibit an anomaly of this nature more strongly than the specific heat itself. We find that the most concentrated alloy has a low-temperature thermal expansion anomaly, which is also detectable in its specific heat. The low-temperature electronic Grüneisen parameter increases with Ni concentration and has a logarithmic singularity in accordance with the theoretical prediction[7] for the mass enhancement. The magnetostriction in the alloys is proportional to the susceptibility enhancement, and the proportionality constant measures the volume derivative of the localized exchange enhancement.

Two samples of Pd were measured. Pd*A* was prepared by arc-melting wire supplied by Matthey-Bishop, and Pd*B* from Pd sponge supplied by Engelhard. The only ferromagnetic impurity detected by spectrochemical analysis was Fe at a level of 4 ppm in Pd*A* and about 10 ppm in Pd*B*. However, the susceptibility measurements show Pd*B* to have appreciable temperature dependence at low temperatures, indicating the presence of undetected magnetic impurities. The Pd:Ni samples were prepared by arc melting from the Matthey-Bishop Pd and annealed for 70 h at 1100 °C at pressures below 10^{-6} Torr. The longitudinal magnetostriction in fields up to 35 kOe and the thermal expansion were measured by a capacitance method. The construction of the capacitance cell is similar to that of the differential cell described by White.[10] The cell is made from Cu which was found to have a negligibly small magnetostriction. The thermal expansion of the cell was calibrated against intrinsic Si, whose thermal expansion was measured absolutely by Sparks and Swenson.[11]

We assume the magnetostriction to be isotropic and write the longitudinal magnetostriction

$$\frac{1}{l}\frac{\partial l}{\partial H}=\frac{1}{3}\frac{1}{V}\frac{\partial V}{\partial H}=\frac{\kappa\chi_A}{3}\frac{\partial \ln\chi_A}{\partial \ln V}H, \tag{1}$$

where κ is the compressibility $V^{-1}(\partial V/\partial p)_T$. The susceptibility χ_A of the localized-exchange-enhancement model for a many-impurity system is[7]

$$\chi_A=\chi_{\mathrm{Pd}}/(1-C\chi_{\mathrm{Pd}}\Delta I_{\mathrm{eff}}), \tag{2}$$

where C is the impurity concentration and χ_{Pd} is the host susceptibility. ΔI_{eff} is the localized exchange enhancement

$$\Delta I_{\mathrm{eff}}=\Delta I/[1-\Delta I\chi_{\mathrm{Pd}}(0)], \tag{3}$$

ΔI being the difference between the impurity and host repulsive potentials and $\chi_{\mathrm{Pd}}(0)$ the susceptibility at the impurity site. Differentiation of Eq. (2) with respect to volume gives the magneto-

Table I. Magnetostriction and thermal expansion of Pd and Pd:Ni alloys.

Sample	$10^6\chi_A(H=0)$ (g^{-1})	$(\partial \ln\chi_A/\partial \ln V)_{H=0}$	m_A/m_{Pd}	γ_A [c]
Pd*A*	6.73	−3.5	1.00	2.77
Pd*B*	7.55	−2.9	1.00	2.77
0.6% Ni	10.6	−1.0	1.13 [a]	3.25
1.0% Ni	14.7	2.7	1.19 [a]	3.7
1.5% Ni	23.8	7.2	1.28 [a]	4.4
1.89% Ni				
4.2°K	40	14.6	1.43 [b]	6.2
1.4°K	47.5	15.3		

[a]Ref. 1.
[b]Our data [see Fig. 3(b)].
[c]The thermal-expansion data for Pd*A* and Pd*B* differ less than their experimental scatter. The resultant average value of the electronic thermal expansion is $\alpha = (53 \pm 3)\times 10^{-10}T$, somewhat greater than the value in the literature (Ref. 13) which was measured for a sample containing 80 ppm of Fe (G. K. White, private communication).

striction of the alloy,

$$\frac{\partial \ln\chi_A}{\partial \ln V} - \frac{\partial \ln\chi_{Pd}}{\partial \ln V} = \left(\frac{\chi_A}{\chi_{Pd}} - 1\right)\left(\frac{\partial \ln\Delta I_{eff}}{\partial \ln V} + \frac{\partial \ln\chi_{Pd}}{\partial \ln V}\right). \tag{4}$$

Since the susceptibility of pure Pd is essentially independent of field H up to 35 kOe, its integrated fractional length change $[l(H)-l(0)]/l(0)$ is quadratic in H from Eq. (1) and provides a measure of $\partial \ln\chi_{Pd}/\partial \ln V$. The Pd:Ni alloys show field dependence of both χ_A and $[l(H)-l(0)]/l(0)H^2$, as one expects for a localized-exchange-enhancement model.[12] Their differential values at zero field and the resultant values of $\partial \ln\chi/\partial \ln V$ from Eq. (1) are adopted for comparison with the theory and are given in Table I. Two values are given for the alloy containing 1.89% Ni, which showed significant temperature dependence at liquid-helium temperatures.

As shown in Fig. 1(a) these results are in fairly good agreement with Eq. (4). They do not give a linear plot when the equation for the single-impurity limit is used instead of Eq. (4). The experimental points in Fig. 1(a) lie near the straight line with slope 4.0, giving $\partial \ln\Delta I_{eff}/\partial \ln V = 7.5$. This large positive value for the volume derivative of the impurity repulsive potential is physically reasonable and is to be contrasted to the small negative value for the volume derivative of the Pd host potential I. Thus if we differentiate the expression for the enhanced susceptibility of Pd,

$$\chi_{Pd} = \frac{N(0)}{1-IN(0)} = \frac{N(0)}{1-\bar{I}}, \tag{5}$$

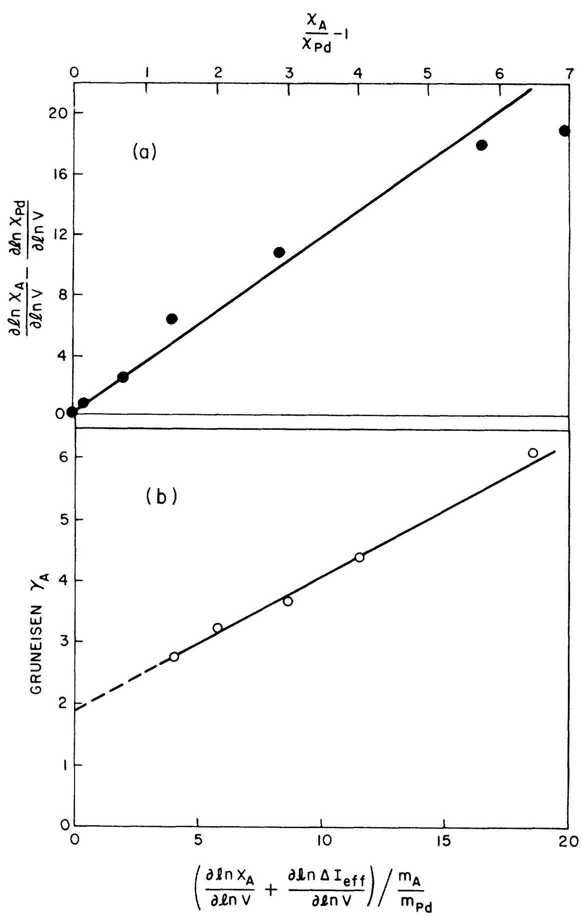

FIG. 1. The magnetostriction and thermal expansion of Pd:Ni alloys. (a) Magnetostriction versus susceptibility enhancement. (b) Electronic Grüneisen parameter versus the ratio of the magnetostriction to the mass enhancement.

we obtain

$$\frac{\partial \ln\chi_{\rm Pd}}{\partial \ln V}=\frac{\partial \ln N(0)}{\partial \ln V}+\frac{\bar I}{1-\bar I}\frac{\partial \ln \bar I}{\partial \ln V}$$
$$=\frac{\partial \ln N(0)}{\partial \ln V}+\frac{\bar I}{1-\bar I}\left(\frac{\partial \ln N(0)}{\partial \ln V}+\frac{\partial \ln I}{\partial \ln V}\right). \quad (6)$$

The volume derivative of the density of states $N(0)$ is about 1.5, a typical value for the electronic Grüneisen parameter for transition metals not having pronounced exchange enhancement,[13] and the enhancement factor $(1-\bar I)^{-1}$ is about 10 for Pd. Substitution of $\partial \ln\chi_{\rm Pd}/\partial \ln V=-3.5$ (Table I) in Eq. (5) gives $\partial \ln I/\partial \ln V\simeq -2$.

We now consider the thermal expansion. Engelsberg, Brinkman, and Doniach[7] show that in the many-impurity system near the critical concentration for ferromagnetism,

$$C_{\rm crit}=(\Delta I_{\rm eff}\chi_{\rm Pd})^{-1}, \quad (7)$$

the mass enhancement is

$$\frac{m_A}{m_0}\simeq\frac{9}{2\sigma}\ln\left(\frac{1}{C_{\rm crit}-C}\right)=\frac{9}{2\sigma}\ln(\Delta I_{\rm eff}\chi_A), \quad (8)$$

where σ is the range parameter for the exchange interaction in the Pd host. Differentiation of Eq. (8) with respect to volume gives the thermal expansion at zero temperature, which we express as an electronic Grüneisen parameter

$$\gamma_A=\frac{\partial \ln N(0)}{\partial \ln V}-\frac{\partial \ln\sigma}{\partial \ln V}+\frac{m_0}{m_A}\frac{9}{2\sigma}\left(\frac{\partial \ln\chi_A}{\partial \ln V}+\frac{\partial \ln\Delta I_{\rm eff}}{\partial \ln V}\right). \quad (9)$$

The values of γ_A $(=3\alpha/\kappa C_v)$ obtained by extrapolation of the linear thermal expansion α of the Pd:Ni alloys to zero temperature are given in Table I. Figure 1(b) shows that our experimental data are in good agreement with Eq. (9). The linear fit has an intercept which gives, with our previous estimate $\partial \ln N(0)/\partial \ln V=1.5$, a value $\partial \ln\sigma/\partial \ln V\simeq -0.5$ for the volume derivative of the range parameter. The slope of the line gives $(m_0/m_{\rm Pd})9/2\sigma=0.22$. This agrees well with the value $(m_0/m_{\rm Pd})9/2\sigma=0.19$ obtained by use of Eq. (8), which we find gives a linear plot using Schindler and Mackliet's low-temperature specific-heat data. Thus both the thermal expansion and the specific heat exhibit a logarithmic singularity in accordance with the theoretical prediction.[7]

There has been considerable interest[7-9] in the possible existence of a low-temperature anomaly in the specific heat, which is caused by the variation of the electron self-energy by virtue of its interaction with spin fluctuations as one moves away from the Fermi surface. Doniach and Engelsberg[4] showed that a term of the form $T^3\ln T$ appears in the uniform-exchange-enhancement model, and the specific heat of strongly paramagnetic Ni:Rh alloys[5] seems to exhibit such an anomaly. The specific heat of Pd:Ni alloys,[1,2] which one might expect to correspond to that of the localized-exchange-enhancement model, was not found to have a low-temperature anomaly. In this model, when impurity scattering is neglected, the specific-heat anomaly near the critical concentration $(\tilde c=C/C_{\rm crit}\lesssim 1)$ is of the form[7]

$$\frac{\Delta C_v}{C_v^{\,0}}=\frac{3\pi^2}{5}\frac{1}{(1-I)(1-\tilde c)}\left(\frac{T}{T_A}\right)^2\ln\left(\frac{T}{T_A}\right), \quad (10)$$

with $T_A=(4/\pi)(1-\bar I)(1-\tilde c)T_{\rm F}$. The corresponding thermal-expansion anomaly $\Delta\alpha/\alpha_0$ is obtained by taking the volume derivative of the entropy. Neglecting the derivative of the slowly varying logarithmic term, we have

$$\frac{\Delta\alpha/\alpha_0}{\Delta C_v/C_v^{\,0}}=\left(\frac{\bar I}{1-\bar I}\frac{\partial \ln\bar I}{\partial \ln V}+\frac{\tilde c}{1-\tilde c}\frac{\partial \ln\tilde c}{\partial \ln V}\right)\gamma_0^{-1}.$$

$$=\left\{\left(\frac{\partial \ln\chi_{\rm Pd}}{\partial \ln V}-\frac{\partial \ln N(0)}{\partial \ln V}\right)+\frac{\tilde c}{1-\tilde c}\left(\frac{\partial \ln\chi_{\rm Pd}}{\partial \ln V}+\frac{\partial \ln\Delta I_{\rm eff}}{\partial \ln V}\right)\right\}\gamma_0^{-1}. \quad (11)$$

We use Eq. (6) and the expression[7] $\tilde c=c\Delta I_{\rm eff}N(0)/(1-\bar I)$ to obtain the latter form of Eq. (11), which

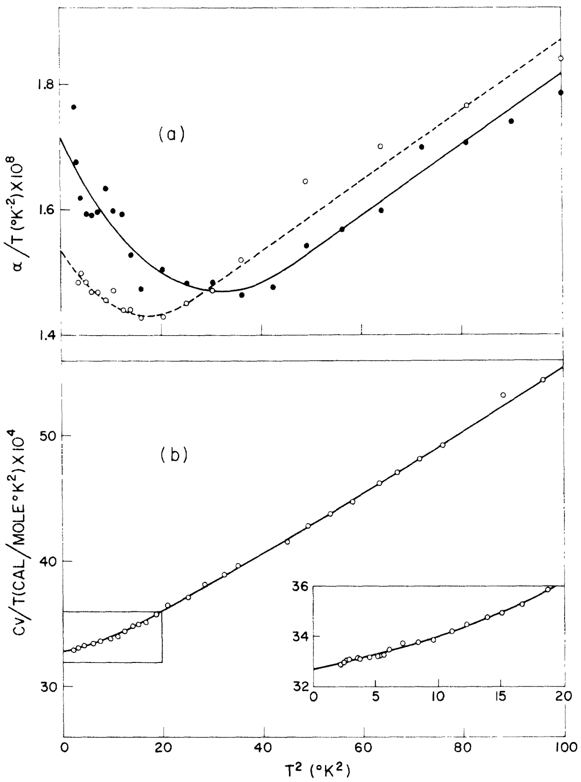

FIG. 2. The thermal expansion and specific heat of the Pd-1.89% Ni alloy. (a) Solid line represents thermal expansion of the annealed sample; dashed line, quenched sample. (b) The specific heat (annealed sample only); the box in the lower right-hand corner is a blowup of the main figure up to $T^2 = 20$.

gives

$$\frac{\Delta\alpha/\alpha_0}{\Delta C_v/C_v^{\,0}} = \frac{-5+4\bar{c}/(1-\bar{c})}{2.8}. \tag{12}$$

The thermal expansion of the most concentrated Pd:Ni alloy [Fig. 2(a)] exhibits a strong anomaly below ~7°K. To explore the possibility that this might be due to concentration fluctuation effects, the sample was remelted and quenched rapidly to enhance any such effects. The anomaly in the quenched sample is in fact somewhat smaller than in the annealed sample [Fig. 2(a)]. The specific heat of the annealed sample [Fig. 2(b)] also shows an anomaly whose magnitude relative to the thermal expansion anomaly is in fairly good agreement with the estimate provided by Eq. (12). These results support Brinkman and Engelsberg's[9] contention that impurity scattering does not eliminate the low-temperature anomaly.

In conclusion, we have shown that in Pd:Ni alloys, (1) the volume derivative of the localized exchange enhancement is large and positive in contrast to the small negative volume derivative of the exchange enhancement in pure Pd, (2) the low-temperature thermal expansion has a logarithmic singularity near the critical concentration like the low-temperature specific heat, and (3) the thermal expansion has a low-temperature anomaly considerably larger than the specific heat anomaly in accordance with the exchange-enhancement theory.

We are grateful to S. Engelsberg for stimulating discussions and to T. R. Kyle for assistance in the measurements.

[1]A. I. Schindler and C. A. Mackliet, Phys. Rev. Letters 20, 15 (1968).

[2]G. Chouteau, R. Fourneaux, K. Gobrecht, and R. Tournier, Phys. Rev. Letters 20, 193 (1968).

[3]N. F. Berk and J. R. Schrieffer, Phys. Rev. Letters 17, 433 (1966).

[4]S. Doniach and S. Engelsberg, Phys. Rev. Letters 17, 750 (1966).

[5]E. Bucher, W. F. Brinkman, J. Maita, and H. J. Williams, Phys. Rev. Letters 18, 1125 (1967).

[6]P. Lederer and D. L. Mills, Phys. Rev. 165, 837 (1968), and Phys. Rev. Letters 20, 1036 (1968).

[7]S. Engelsberg, W. F. Brinkman, and S. Doniach, Phys. Rev. Letters 20, 1040 (1968).

[8]P. Fulde and A. Luther, Phys. Rev. 170, 570 (1968).

[9]W. F. Brinkman and S. Engelsberg, following Letter [Phys. Rev. Letters 21, 1187 (1968)].

[10]G. K. White, Cryogen. 1, 151 (1961).

[11]P. W. Sparks and C. A. Swenson, Phys. Rev. 163, 779 (1967).

[12]S. Doniach, to be published.

[13]J. G. Collins and G. K. White, in Progress in Low Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, The Netherlands, 1964), Vol. IV.