almost identical to ours.

[15]Structure in conductance curves caused by molecular vibrations in the oxide barrier [R. C. Jaklevic and J. Lambe, Phys. Rev. Letters 17, 1139 (1966)] is usually very weak and is symmetrical in bias voltage.

[16]Recent tunneling experiments with bulk Bi have failed to reproduce the data of Esaki and Stiles. [I. Giaver, International Conference on Tunneling in Solids, Risø, Denmark, 1967 (to be published)].

SPECIFIC-HEAT ENHANCEMENT IN STRONGLY PARAMAGNETIC Pd:Ni ALLOYS

A. I. Schindler and C. A. Mackliet
United States Naval Research Laboratory, Washington, D. C. 20390
(Received 1 November 1967)

It has been recently suggested[1,2] that, in strongly exchange-enhanced paramagnetic metals and alloys, a large renormalization of the d-electron mass results from paramagnon interactions; this effect becomes increasingly large as the alloy composition approaches that at which ferromagnetism occurs. Several recent calculations[3,4] for the paramagnon enhancement of the bare band mass m yield

$$m^*/m = 1 + \tfrac{9}{2}\ln\{\tfrac{1}{3}[1/(1-\bar{I})]\}, \quad (1)$$

where m^* is the enhanced electron mass at zero temperature and $\bar{I}$ represents a semiphenomenological short-range repulsion between the fermions.[5] This enhancement of the effective mass is observed as an increase in the linear term of the low-temperature specific heat. Doniach, Engelsberg, and Rice[2] have shown further that if one carries out the theoretical calculation at higher temperatures, the specific heat will have an additional term of the form $T^3\ln(T/\bar{T}_F)$, where $\bar{T}_F$ is a characteristic paramagnon temperature.

The method that has been used to test the mass enhancement theory is that of examining the low-temperature specific heat of a concentrated alloy system[3] in which the strength of the electron-electron interactions is a strong function of composition. The strength of these interactions may be estimated from the Stoner enhancement factor (S) of the paramagnetic spin susceptibility. One can write $S = \chi_{spin}/\chi_0 = (1-\bar{I})^{-1}$, where χ_{spin} is the spin-only part of the measured susceptibility and χ_0 is the value of the Pauli susceptibility calculated from the bare-band density of states. Since for the metals and alloys of interest we do not know to sufficient accuracy either χ_{spin} or χ_0, we can generally only make reasonable estimates for the value of S. However, one can examine a nearly ferromagnetic alloy system over a region of composition in which the paramagnetic susceptibility increases rapidly as the critical composition for the occurrence of ferromagnetism is approached. If one can be sure that no local-moment formation has occurred and that the density of states of the alloy has not been changed drastically by alloying additions, then it would appear safe to presume that $\bar{I}$ is monotonically and rapidly increasing with alloying. Little change in the density of states upon alloying is likely to occur if only small alloying additions are needed to produce ferromagnetism. On the other hand, for a series of concentrated alloys one must have independent evidence that the changes in the observed parameters are not the result of drastic changes in the density of states resulting from alloying.

An ideal system in which to test the exchange enhancement theories is that of dilute alloys of Ni in Pd. Palladium is well known as an exchange-enhanced metal; S has been estimated at values ranging from 8 to 50.[6] If one adds only about 2.25 at.% Ni, the system goes ferromagnetic,[7] i.e., $S \to \infty$. Therefore, for compositions between 0 and 2.25 at.% Ni, S will have values ranging from approximately 10 to ∞.

Measurements of the susceptibility do not seem to indicate any complicating local-moment phenomena,[8] and the Pd:Ni system forms an uninterrupted series of solid solutions in which no atomic ordering occurs. Although the density-of-states curve for Pd in the vicinity of the Fermi energy decreases with increasing energy,[9] it is unlikely that significant changes in the density of states at the Fermi level occur as 2 at.% Ni or less is added.

In addition, measurements of the low-temperature electrical resistivity of paramagnetic alloys of Ni in Pd have been made[10] which

confirm both the existence of paramagnons and the suitability of the Pd:Ni system for the testing of enhancement-effect theories.

However, Lederer and Mills[11] have shown that the concept of a spatially averaged value of $\bar{I}$ obtained from values of S calculated from the magnetic susceptibility is inappropriate for dilute alloys of Ni in Pd. They have introduced the notion of local enhancement in very 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, for compositions of Ni greater than about 1% the Lederer and Mills local-enhancement calculation does not apply.

In order to test exchange-enhancement theories, we have carried out measurements of the low-temperature specific heat for a series of Pd:Ni specimens containing 0.47, 0.97, 1.66, and 1.95 at.% nickel. The specimens consisted of roughly $\frac{1}{2}$ to $\frac{3}{4}$ mole of alloy and were, in fact, right circular sections of the ingots from which material was taken for preparation of the wires used in the above-mentioned resistivity work. Measurements were made in a conventional manner using apparatus described earlier.[12]

The present specific-heat data consisted of measurements at 16 temperatures in the range 2.0 to 4.2°K for the 0.47-at.% Ni specimen, at 36 temperatures in the range 1.6 to 4.2°K for the 0.97-at.% Ni specimen, at 40 temperatures in the range 1.125 to 4.2°K for the 1.66-at.% Ni specimen, and at 47 temperatures in the range 1.132 to 4.2°K for the 1.95-at.% Ni specimen. The data shown in Fig. 1 (excluding the cluster of points at the lowest temperatures) are typical, both in regard to the degree of scatter and in regard to the practice of usually taking data in clusters of four points at very closely spaced temperatures.

The procedure to be used in analyzing the experimental data and the parameters to be derived from the analysis will depend critically on the precise manner in which the specific heat C varies with the absolute temperature T. The present data were plotted in the usual C/T-vs-T^2 format, and it was found that a straight-line relationship was clearly indicated, to within the accuracy of the measurements and excluding a few very low-temperature points whose significance will be considered later. The data shown in Fig. 1 (excluding the 7-point cluster at the lowest temperatures) are typical.

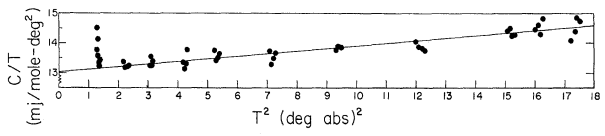

FIG. 1. Specific heat of a Pd-1.95 at.% Ni specimen.

Since the theory predicts the occurrence of a $T^3\ln(T/\bar{T}_F)$ term in the specific heat, it is pertinent to consider the only results of the present investigation which give even a suggestion of an atypical temperature dependence of the specific heat. The data in question are the badly scattered cluster of points that occur at the lowest temperatures for the 1.95-at.% Ni specimen, as shown in Fig. 1. (A similar, though less pronounced, effect was observed for the 1.66-at.% Ni specimen; measurements at such low temperatures were not made for the other two specimens.) In regard to the points in question, it may be mentioned that the raw data for these measurements showed no unusual features, and that measurements made in the past (with the present apparatus) on other specimens at similar low temperatures showed neither such large scatter nor such atypically large values of C/T. It therefore seems possible that the points in question are indicative of a real effect, although no explanation can currently be offered. (Further investigation of this matter is under way.)

However, even if these points are assumed to be a valid indication of an unusual increase in C at low temperatures, the present data still cannot be fitted by means of a relation of the form $C/T=\gamma+\beta T^2+\alpha T^2\ln(T/\bar{T}_F)$. These experimental results are in clear disagreement both with the above-mentioned theory and with the experimental results reported by Bucher, et al.,[3] since the present 1.95-at.% Ni specimen has a Stoner enhancement factor of approximately 80,[13] whereas the Ni:Rh specimen which showed a large $T^3\ln(T/\bar{T}_F)$ term in the Bucher investigation had an enhancement factor estimated at ~70.

Since there appears to be no basis for any alternative procedure, the present data have been analyzed in terms of the usual relation, $C/T=\gamma+\beta T^2$. Values of γ obtained by least-

Table I. A comparison of the values of γ experimentally determined with those predicted from theory.

Composition	χ_{4° (10^{-6} emu/g)	γ_{exp} (mJ/mole deg^2)	$(\gamma_{alloy}/\gamma_{Pd})_{exp}$	$(\gamma_{alloy}/\gamma_{Pd})_{calc}$
Pd	7.25	9.38	1	1
Pd-0.47% Ni	11.07	10.46	1.12	1.29
0.97% Ni	17.33	11.09	1.18	1.62
1.66% Ni	35.15	12.29	1.31	2.11
1.95% Ni	60[a]	13.04	1.39	2.48

[a]This value of susceptibility has been obtained from the susceptibility data given in Ref. 8.

squares calculations are given as a function of composition in Fig. 2. The results are shown on the left in an expanded scale and then on the right with the results of earlier investigations. (References for the earlier data appear in Ref. 12.) It is quite clear that γ is an extremely sensitive function of composition and increases by over 40% for a nickel addition of only 2 at.%. On the other hand, γ does not increase nearly as rapidly as Eq. (1) would suggest.[5] Values of $\gamma_{alloy}/\gamma_{Pd}$ have been calculated from Eq. (1) using an assumed Stoner enhancement factor of 10 for pure Pd and using the 4.2°K susceptibility data obtained for these samples by Mr. G. Williams of Imperial College, London, England. The calculated results appear in Table I along with the experimental data.

In conclusion, the results of the present investigation reveal a sharp increase in γ with increased Ni content, although the rate of increase is less rapid than that predicted theoretically by the uniform-enhancement model; in addition, there is no evidence for a $T^3 \ln(T/\overline{T}_F)$ term in the low-temperature specific heat.[14]

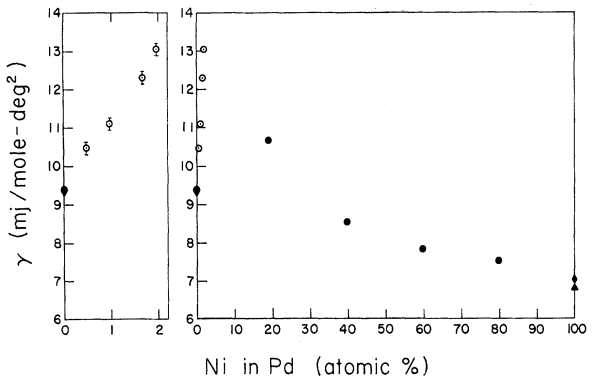

FIG. 2. Electronic specific-heat coefficient γ as a function of composition for Pd:Ni alloys. Open circles show present results. Solid points show results of earlier investigations (see Ref. 12 for further references).

Although the experimental results obtained here are in qualitative agreement with the various mass-enhancement theories, it would be prudent to point out that the rapid increase in γ might yet be shown to come about from a straightforward band effect (even if electron-phonon interactions are not invoked). According to the most recent band calculations,[9] the Fermi level of palladium is just beyond the maximum in the curve of density-of-states of the hybridized d–s band versus energy. Since the number of holes in Pd is[15] 0.36 per atom while that of Ni is approximately 0.6, we might expect that, as Ni is added to Pd, the Fermi level of the alloy would shift to lower energies and thereby sample higher densities of states.

The authors would like to thank J. R. Schrieffer and D. L. Mills and P. Lederer for copies of their papers prior to publication, B. C. La Roy for valuable help in sample preparation, O. R. Gates for chemical analysis, E. J. Brooks for x-ray fluorescence analysis, and G. Williams for measurements of the magnetic susceptibility of the specimens.

[1]N. F. Berk and J. R. Schrieffer, Phys. Rev. Letters 17, 433 (1966), and in Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, USSR, 1966 (to be published).

[2]S. Doniach and S. Engelsberg, Phys. Rev. Letters 17, 750 (1966); S. Doniach, S. Engelsberg, and M. J. Rice, in Proceedings of the Tenth International Conference on Low Temperature Physics, Moscow, USSR, 1966 (to be published).

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

[4]J. R. Schrieffer, in Proceedings of the International Congress on Magnetism, Boston, Massachusetts, 1967 (to be published).

[5]Equation (1) is the result of a calculation which only

considers the simplest case of an electron-electron interaction in a single spherical band. The predicted mass enhancement can be decreased significantly by the introduction of Hund's rule (intra-atomic exchange) [S. Doniach, Phys. Rev. Letters 18, 554 (1967)], and finite-range (inter-atomic) exchange interactions [Bucher et al., Ref. 3, and J. R. Schrieffer, Phys. Rev. Letters 19, 644 (1967)], but the relative strengths of these two latter interactions have not yet been determined.

[6]S. Foner, R. Doclo, and E. J. McNiff, Jr., in Proceedings of the International Congress on Magnetism, Boston, Massachusetts, 1967 (to be published).

[7]R. M. Bozorth, D. D. Davis, and J. H. Wernick, J. Phys. Soc. Japan Suppl. B-1, 112 (1962).

[8]D. Shaltiel, J. H. Wernick, H. J. Williams, and M. Peter, Phys. Rev. 135, A1346 (1964).

[9]L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).

[10]A. I. Schindler and B. R. Coles, in Proceedings of the International Congress on Magnetism, Boston, Massachusetts, 1967 (to be published); A. I. Schindler and M. J. Rice, Phys. Rev. 164, 759 (1967).

[11]P. Lederer and D. L. Mills, to be published.

[12]C. A. Mackliet and A. I. Schindler, J. Phys. Chem. Solids 24, 1639 (1963).

[13]This estimate was obtained using the susceptibility data of Shaltiel et al. (Ref. 8) plus an assumed Stoner enhancement factor 10 for pure Pd.

[14]A very recent calculation for the initial (Ni concentration <1%) increase of the specific-heat coefficient γ, again based upon the local enhancemement model, has been made by P. Lederer and D. L. Mills, to be published. They have deduced a value of $\gamma^{-1}(d\gamma/dc) \approx 17$, in good agreement with our experimentally determined value of ~19. They also have shown theoretically that for dilute alloys the local-enhancement model yields a T^3 term as the first correction to the linear term in the specific heat—in contrast with the $T^3 \ln T$ term predicted for the case of uniform enhancement.

[15]J. J. Vuillemin, Phys. Rev. 144, 396 (1966).

SURFACE SPIN-FLOP STATE IN A SIMPLE ANTIFERROMAGNET*

D. L. Mills
Department of Physics, University of California, Irvine, California
(Received 13 October 1967)

It is well known that in antiferromagnetic materials, a magnetic field applied parallel to the direction of the sublattice magnetization may result in an instability of the ground state, if the strength H of the external field exceeds the value $H_c^{(B)} = (2H_E H_A)^{\frac{1}{2}}$, at $T = 0$. Within the framework of the molecular field approximation, it is not difficult to see that when $H > H_c^{(B)}$, the state sketched in Fig. 1(b) has an energy lower than that of the antiferromagnetic (AF) ground state illustrated in Fig. 1(a). The presence of the spin-flop instability may also be inferred by noting that as $H \to H_c^{(B)}$, the excitation energy of the $\vec{k} = 0$ bulk magnon with frequency $(2H_E H_A)^{1/2} - H$ sinks to zero. Foner[1] has provided a discussion of this "spin-flop" transition, along with a review of a number of experimental studies.

We have recently completed an investigation of the properties of surface magnons in a two-sublattice antiferromagnet of the CsCl structure, with a free (100) surface. A detailed discussion of the properties of these modes, along with their influence on the low-temperature properties of the system, will be given elsewhere.[2] For the present discussion, it is sufficient to note that at $k = 0$, the frequency of the (nondegenerate) surface mode is $(H_E H_A)^{1/2}$, provided surface pinning fields and changes in exchange constants near the surface are neglected and $H_E \gg H_A$. The effect on this result of changes in H_A and H_E near the surface is expected to be small, under conditions described in detail below. If a field H is applied antiparallel to the anisotropy field H_A seen by the surface spins, the excitation energy of the surface mode decreases to $(H_E H_A)^{1/2} - H$. For $H > H_c^{(s)} = (H_E H_A)^{\frac{1}{2}}$, the excitation energy of the surface mode becomes negative. By pursuing the arguments given above for

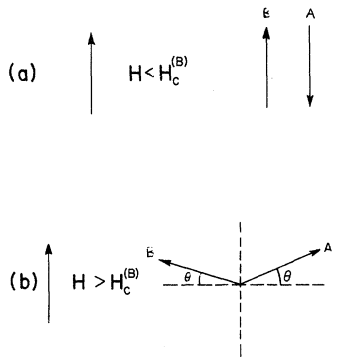

FIG. 1. (a) The bulk AF ground state when $H < H_c^{(B)}$. (b) The ground state for $H > H_c^{(B)}$; $e = H/2H_E$.