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Specific Heat and Electrical Resistivity of Exchange-Enhanced Dilute *Pt*-Ni Alloys

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Experimental measurements of the specific heat and electrical resistivity of dilute *Pt*-Ni alloys have been made at temperatures from ~1.2 to 4.2°K. Specimen compositions were 1.0-, 3.4-, 7.7-, and 12.8_5-at.% Ni for the specific-heat work and 0.67-, 1.3-, 2.0-, 4.0-, and 9.4-at.% Ni for the resistivity work. The specific-heat data for each alloy are well fitted by a relation of the form $C=\gamma T+\beta' T^3$, the resistivity data by a relation of the form $\rho=\rho_0+AT^2$. The dependence of γ, β', and A upon the Ni concentration c may be expressed as follows: $\gamma^{-1}d\gamma/dc\simeq 3$ over the entire range of composition investigated; for the lower concentrations only, $(1/\beta')(d\beta'/dc)\sim -3$ to -7 and $A^{-1}dA/dc\simeq 28$. The experimental results are used to evaluate current theories of localized spin-fluctuation effects; qualitative agreement is good, although quantitative agreement is very limited.

INTRODUCTION

THE electronic properties of exchange-enhanced transition metals and transition-metal alloys have been of substantial theoretical[1–8] and experimental[3,8–12] interest in recent years. Several examples of particularly interesting experimental observations include (1) the very strong concentration dependence of the low-temperature electronic specific heat of Rh-Ni alloys[9] and of dilute *Pd*-Ni alloys[10,11,8]; (2) the anomalous temperature dependence of the low-temperature specific heat of certain Rh-Ni alloys[9]; and (3) the dominance and strong concentration dependence of a T^2 term in the low-temperature electrical resistivity of dilute *Pd*-Ni alloys.[3] Theoretical interpretations[13] of the above (and other important) experimental results have been given in terms of persistent-spin-fluctuation effects; two closely related (but conceptually distinct) theories have been developed.

One theory, the "uniform enhancement" theory,[2,3,14] assumes that the short-range intra-atomic Coulomb repulsion between d electrons is the same everywhere in the solid. This work is specifically applicable to exchange-enhanced pure metals and has been extended to the case of concentrated alloys by assuming that the strength of the electronic repulsion is a function of alloy composition (but is nevertheless the same everywhere in the solid).

A second theory, the "local enhancement" theory,[4,6,7] has been developed specifically for the case of a host matrix containing a single impurity atom. The basic interelectronic interaction in this case is assumed to be particularly large in the cell containing the impurity atom. Appreciable short-range intra-atomic repulsions between d electrons elsewhere in the solid may or may not be taken into account, depending on the nature of the host matrix. This work may be readily applied to alloys in the dilute limit; an extension[7] to the case of more concentrated alloys has been carried out for certain systems.

More recent theoretical work has dealt with a number of important related problems, including (1) *inter*atomic exchange interactions[15] between electrons, (2) Hund's rule coupling[15–17] between electrons, (3) band-structure effects,[5,15,16] and (4) impurity scattering effects.[18,19]

Since current theories of spin-fluctuation effects involve various highly simplified models as well as a number of nontrivial analytical approximations and assumptions, it is useful to provide additional experimental data for use in evaluating these theories. The present work on the specific heat and electrical resistivity of dilute *Pt*-Ni alloys has been carried out with this aim in mind.

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

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

[3] A. I. Schindler and M. J. Rice, Phys. Rev. **164**, 759 (1967).

[4] P. Lederer and D. L. Mills, Phys. Rev. **165**, 837 (1968).

[5] J. R. Schrieffer, J. Appl. Phys. **39**, 642 (1968).

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

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

[8] G. Chouteau, R. Fourneaux, R. Tournier, and P. Lederer, Phys. Rev. Letters **21**, 1082 (1968).

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

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

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

[12] E. Fawcett, E. Bucher, W. F. Brinkman, and J. P. Maita, Phys. Rev. Letters **21**, 1183 (1968).

[13] There appears to be some evidence for the occurrence of "giant magnetization clusters" in ferromagnetic Ni-Rh alloys [see T. J. Hicks, B. Rainford, J. S. Kouvel, G. G. Low, and J. B. Comly, Phys. Rev. Letters **22**, 531 (1969)]; it is suggested in this paper that this phenomenon may occur in all highly exchange-enhanced alloy systems. If such behavior should indeed occur, then the interpretation of various low-temperature properties would probably be significantly affected.

[14] W. F. Brinkman and S. Engelsberg, Phys. Rev. **169**, 417 (1968).

[15] J. R. Schrieffer, Phys. Rev. Letters **19**, 644 (1967).

[16] S. Doniach, Phys. Rev. Letters **18**, 554 (1967).

[17] B. Caroli, P. Lederer, and D. Saint-James, Phys. Rev. Letters **23**, 700 (1969).

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

[19] W. F. Brinkman and S. Engelsberg, Phys. Rev. Letters **21**, 1187 (1968).

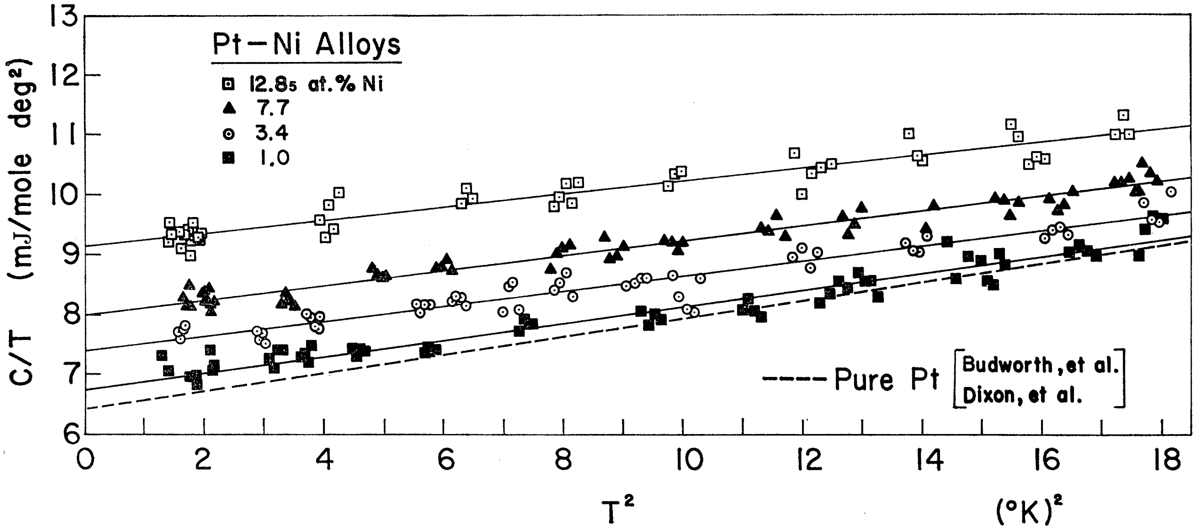

FIG. 1. Specific heat of dilute *Pt*-Ni alloys at low temperatures. (See Ref. 26 in regard to data for pure Pt.)

EXPERIMENTAL DETAILS

The more important details of specimen preparation and characterization will be mentioned briefly. It may first be noted that the specific-heat specimens and the resistivity specimens were prepared and handled completely independently at all stages of the work; however, the constituent materials, methods of preparation, and resultant characteristics for the two sets of specimens were similar in several respects and a unified discussion of these points is appropriate.

High-purity (99.999+%) Pt powder and Ni rod were induction melted under argon, using high-purity recrystallized alumina crucibles for the specific-heat specimens and fused silica crucibles for the resistivity specimens. One specific-heat specimen (1.0-at. % Ni) and two resistivity specimens (4.0- and 9.4-at. % Ni) were prepared separately; all other specific-heat specimens were prepared from the 1% (or succeeding) specimens by appropriate additions of Ni, whereas all other resistivity specimens were prepared from the 4% (or succeeding) specimens by appropriate additions of Pt. All melts yielded cylindrical ingots—roughly $\frac{1}{2}$-in. diameter and $\frac{1}{2}$ in. long for the specific-heat specimens and roughly $\frac{5}{32}$-in. diameter and $\frac{1}{4}$ in. long for the resistivity specimens. The former were each, in turn, pressed in a hydraulic press to yield the flat faces needed for the specific-heat specimen holder employed, whereas the latter specimens were each, in turn, subjected to appropriate swaging and drawing (as well as intermediate annealing) operations to yield the wires needed in the resistivity work. All specimens were finally cleaned and annealed before measurements were made. A 20-h anneal at 1200°C under argon was employed for the resistivity specimens and a several hour anneal at 900–1000°C under vacuum was employed for the specific-heat specimens.

The chemical compositions of the specimens are given in Tables I and II; these values were determined by means of wet-chemical and/or x-ray fluorescence analyses. The latter technique was also used to check compositional homogeneity; only in the 7.7-at. % Ni specimen was inhomogeneity detected. The uncertainties in composition quoted in Tables I and II are conservative estimates based on the probable limitations of the analytical procedures and, in the case of the 7.7-at. % Ni specimen, on the extent of compositional inhomogeneity as well.

Specimen purity was determined by means of spectrographic analysis. In the case of the specific-heat speci-

TABLE I. Specific heat of *Pt*-Ni alloys.

Ni Concentration (at. %)	γ (mJ/mole °K²)	β' (mJ/mole °K⁴)
$1.0\pm0.1_5$	6.76 ± 0.09	0.136 ± 0.009
3.4 ± 0.2	7.39 ± 0.11	0.124 ± 0.011
7.7 ± 0.5	7.99 ± 0.07	0.122 ± 0.007
$12.8_5\pm0.2_5$	9.13 ± 0.11	0.110 ± 0.011

TABLE II. Electrical resistivity of *Pt*-Ni alloys.

Ni Concentration (at. %)	A (10^{-12} Ω cm/°K²)	ρ_0 (10^{-9} Ω cm)
0	15.4 ± 0.6	8.021 ± 0.006
0.67 ± 0.07	19.7 ± 1.1	553.477 ± 0.012
1.3 ± 0.1	21.3 ± 1.2	$1{,}134.706\pm0.011$
$2.0\pm0.1_5$	24.6 ± 1.2	$1{,}645.594\pm0.012$
$4.0\pm0.1_5$	32.7 ± 1.6	$3{,}182.220\pm0.016$
9.4 ± 0.2	52.2 ± 2.2	$7{,}261.062\pm0.023$

mens, the main impurities were found to be Fe, Si, and Al. The concentration of Fe in these specimens was typically a few hundred ppm, whereas the concentrations of Si and Al were each in the 10–100 ppm range. The resistivity specimens showed impurity concentrations of less than about 10 ppm for any of the various elements that were detected, the sole exception being that the 9.4-at. % Ni specimen showed a Si concentration in the 10–100 ppm range.

The specific-heat specimens had masses of roughly 60–65 g (or approximately $\frac{1}{3}$ mole). The resistivity specimens were approximately 0.015-in. diameter and ~3 in. long.

The experimental procedures and equipment used in the specific-heat work have been described elsewhere.[20] The resistivity measurements were made by standard potentiometric methods employing a six-dial thermofree potentiometer and a photoelectric galvanometer.

EXPERIMENTAL RESULTS

Specific Heat

Specific-heat measurements in the 1.15–4.2°K range have been carried out for a series of *Pt*-Ni alloys having the compositions listed in Table I. All individual data points have been plotted in Fig. 1, in the usual C/T-versus-T^2 format. It is clear from these plots that the present data exhibit only the simple temperature dependence which is usually found for the specific heat of metals at low temperatures, namely, $C(T)=\gamma T+\beta' T^3$, where γ and β' are constants whose values depend upon alloy composition (and whose interpretation depends on the nature of the system and the particular theory invoked). The basic data have accordingly been analyzed in terms of the above relationship; the "least-squares" values of γ and β', along with their calculated statistical uncertainties (95% confidence level), are given in Table I and Figs. 2 and 3.

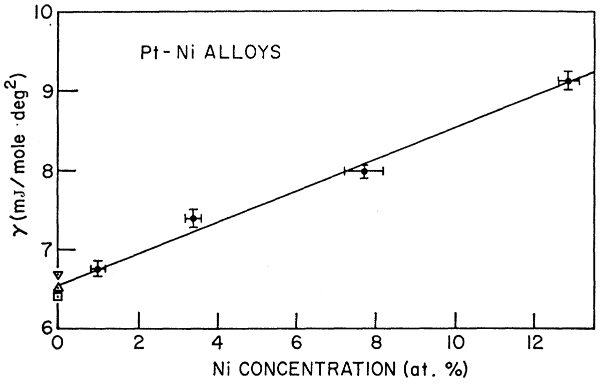

FIG. 2. Concentration dependence of the electronic specific-heat coefficient for dilute *Pt*-Ni alloys. (See Ref. 26 in regard to data for pure Pt.)

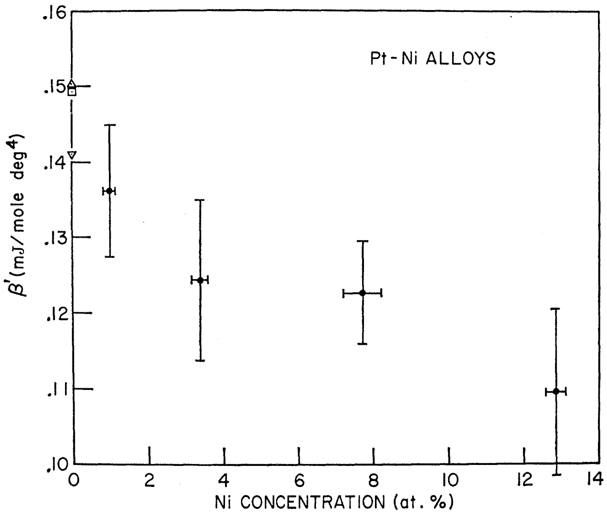

FIG. 3. Concentration dependence of the coefficient of the T^3 term in the low-temperature specific heat of dilute *Pt*-Ni alloys. (See Ref. 26 in regard to data for pure Pt.)

In addition to the above noted explicit temperature dependence, several other significant and unambiguous features of the present experimental results may be emphasized: (1) The electronic specific-heat coefficient γ increases essentially linearly with increasing Ni concentration c; the data yield $[1/\gamma(\text{Pt})][d\gamma(\text{alloy})/dc]\cong 3$, over the range of concentration investigated; (2) the coefficient β' of the T^3 term in the low-temperature specific heat decreases significantly with increasing Ni concentration; the data yield only the rather rough estimate that, for the lower concentrations, $[1/\beta'(\text{Pt})]\times[d\beta'(\text{alloy})/dc]\sim -3$ to -7.

Electrical Resistivity

Electrical-resistivity measurements in the 1.3–4.2°K range have been made for pure Pt and for a series of *Pt*-Ni alloys having the compositions listed in Table II. The basic $\rho(T)$ data are given in a convenient form in Fig. 4 and have been analyzed by means of the relationship $\rho(T)=\rho_0+AT^2$, where ρ_0 and A are constants whose magnitudes depend upon alloy composition. (An attempt was made to fit the present data by including a T^5 lattice contribution[21] in addition to the two given terms. However, the values of the coefficient of this term obtained thereby were not statistically different from zero for any of the resistivity specimens, and such a term was therefore not employed in fitting the present data.) Values of ρ_0 and A, as determined by a computer program for "least-squares" curve fitting, are given in Table II, along with the 95% confidence-level uncertainties.

The parameters ρ_0 and A are plotted as functions of composition in Fig. 5. It may be observed that A

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

[21] R. J. Berry, Can. J. Phys. **45**, 1693 (1967).

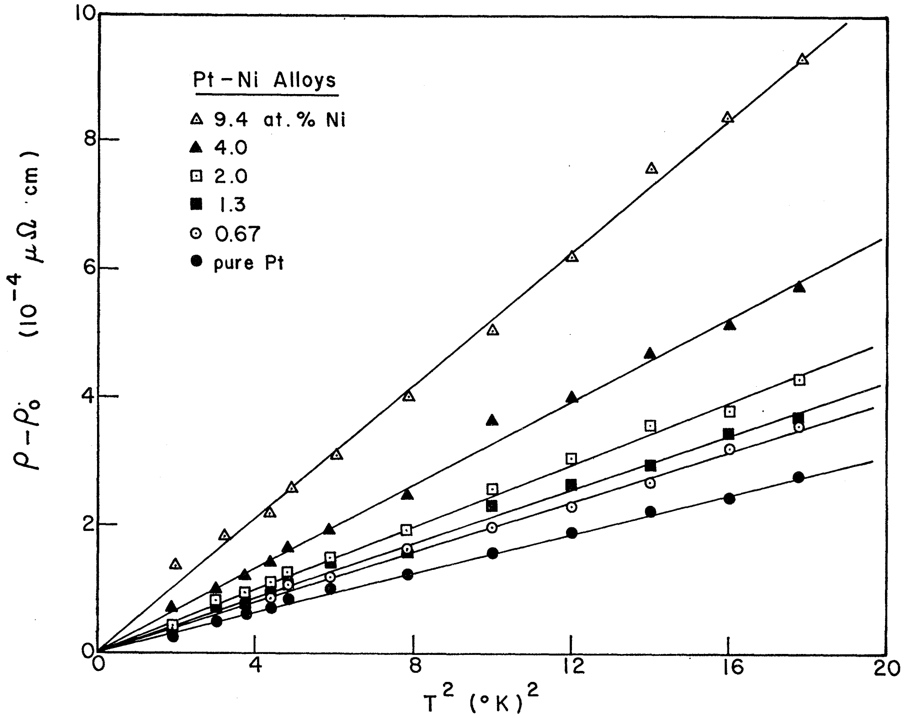

FIG. 4. Electrical resistivity of dilute *Pt*-Ni alloys at low temperatures.

increases strongly with increasing Ni concentration; the data for the lower concentrations yield $[1/A(\text{Pt})]\times[dA(\text{alloy})/dc]\sim 28$. (It may also be observed that ρ_0 is a very smooth function of composition; this behavior is entirely consistent with the previously quoted high specimen-purity and alloy-composition determinations.)

Finally, it should be mentioned that the error in the determination of the form factor for any given specimen has been estimated as approximately 3%, whereas the quoted statistical uncertainties range from approximately 4 to $5\frac{1}{2}$% for the values of A and from approximately 0.1 to 0.0003% for the values of ρ_0.

DISCUSSION

Since the *Pt*-Ni (transition-metal) alloys which have been investigated are of the exchange-enhanced type, the persistent spin-fluctuation theories mentioned in the Introduction are directly applicable (in the appropriate form, of course), and the present experimental results will be considered mainly in relation to those theories.

And, in view of the comparative diluteness of all alloys examined, it seems clear that the *local* enhancement theory should be applicable, particularly to the results obtained at the lower concentrations. But before proceeding to a detailed comparison of theory and experiment, it may be noted that the nature of the theoretical predictions depends significantly upon whether or not the host matrix itself is assumed to be exchange enhanced. Since pure Pt is apparently only rather moderately exchange enhanced (the Stoner factor[22] is $\cong 5/3$), it may be appropriate to consider the theoretical predictions obtained for both alternatives (i.e., both with and without host enhancement) in those cases where such calculations have been made.

Specific Heat

The effect of strong local exchange enhancement upon the electronic specific heat of dilute transition-metal alloys was first considered by Lederer and Mills.[6] They dealt with the single-impurity case and assumed, in particular, that the intra-atomic repulsion between d electrons was especially large in the cell containing the impurity atom, but was insignificant elsewhere. Their calculation yielded the prediction that the linear term in the low-temperature electronic specific heat of dilute alloys would increase strongly with increasing impurity concentration. (They also noted that the first correction to the linear specific-heat term would be proportional to T^3, but they gave no details.) Their detailed prediction (for the previously noted case of no exchange enhancement in the host matrix) may be expressed as follows:

$$\xi\equiv\frac{1}{\gamma(\text{host})}\frac{d\gamma(\text{alloy})}{dc}\bigg/\frac{1}{\chi(\text{host})}\frac{d\chi(\text{alloy})}{dc}=\frac{3n(0)}{2n^*(0)},$$

where γ is the coefficient of the linear term in the low-temperature specific heat, χ is the spin suscepti-

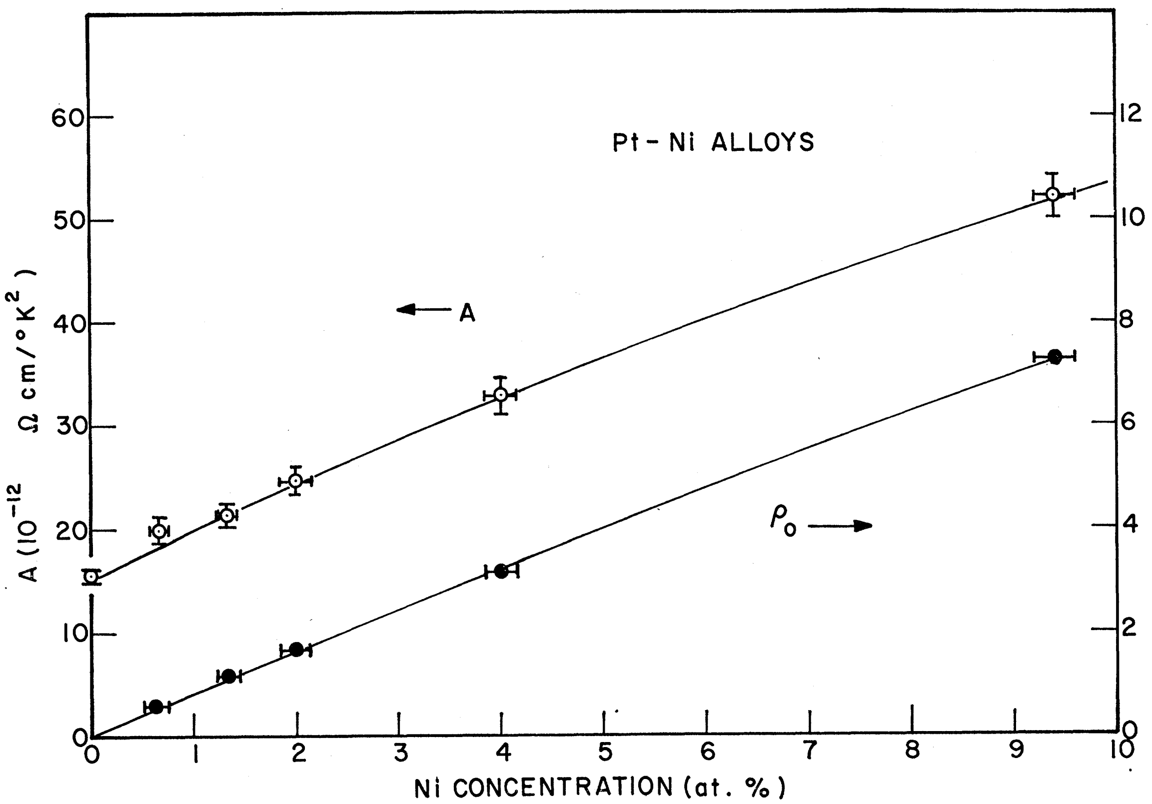

FIG. 5. Concentration dependence of the residual resistivity and of the coefficient of the T^2 term in the low-temperature electrical resistivity of dilute *Pt*-Ni alloys.

bility, c is the concentration of impurity atoms, $n(0)$ is the bare band density of states at the Fermi level, and $n^*(0)$ is the observed specific-heat density of states of the host.

In comparing theory and experiment, it may be noted that a strong increase in γ with increasing impurity concentration *is* observed experimentally—in qualitative agreement with the theory. But quantitative agreement is very poor, as the following calculations show. The present experimental results for γ of *Pt*-Ni alloys, plus the results of other investigators[23] for the magnetic susceptibility of dilute *Pt*-Ni alloys, yield $\xi = 0.25$ to 0.285, whereas the value of n^*/n obtained in recent band calculations[22] for Pt yields $3n(0)/2n^*(0) = 1.5/1.46 \simeq 1$. The numerical discrepancy between the experimentally obtained and the theoretically calculated values of ξ is thus rather large. However, it is expected[6] that $3n/2n^*$ will constitute an upper limit for ξ in those systems in which exchange enhancement in the host *is* important. Thus, in a very restricted sense, the theory and experiment may at least be said to be consistent, quantitatively.

The local-enhancement theory has also been applied to the case in which exchange enhancement of the host matrix *is* considered important. Two different calculations have been carried out, one by Engelsberg *et al.*[7] and one by Chouteau *et al.*[8] Although these calculations are basically very similar, they differ significantly in several respects and will be considered separately.

The calculation of Engelsberg *et al.*[7] for local-enhancement effects in a significantly exchange-enhanced host predicts important changes in the temperature dependence of the low-temperature electronic specific heat. They find, in part, that the linear term $[\gamma T]$ will be modified such that

$$\xi \equiv \frac{1}{\gamma}\frac{d\gamma}{dc} \Big/ \frac{1}{\chi}\frac{d\chi}{dc} = \left(\frac{m^*}{m}\right)^{-1}_{\text{host}} \times \tfrac{3}{2}(\kappa_0{}^2 + \tfrac{1}{3}\bar{I}\sigma)^{-1},$$

where γ, χ, and c are defined above; m^*/m is the mass enhancement factor for the host; $\kappa_0{}^2$ is the reciprocal of the Stoner enhancement factor for the host; $\bar{I} \equiv 1 - \kappa_0{}^2$; and σ is a range parameter for the host interaction.[7] On the basis of the present experimental data for γ and the previously quoted experimental

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[22] F. M. Mueller, J. W. Garland, M. H. Cohen, and K. H. Bennemann (unpublished).

[23] The authors are grateful to A. Thorpe and S. Sullivan, of Howard University, for making magnetic-susceptibility measurements on a number of specimens cut from the same wire as the present resistivity specimens; these investigators's results yield $(1/\chi)(d\chi/dc) \simeq 12$. More recent work, by H. Launois [thesis, University of Paris, 1969 (unpublished)], yield $(1/\chi)(d\chi/dc) = 10.6 \pm 2.6$.

data[23] for χ of *Pt*-Ni alloys, and with $m^*/m \cong \frac{3}{2}$ and $\bar{I} \simeq \frac{2}{5}$ (Ref. 22), the above relationship will be satisfied for $\sigma \sim 25$. This value may be compared with the value of 13 obtained for *Pd*-Ni alloys by Engelsberg *et al.*[7] and with the value of 6 obtained[7,24] for pure Pd. (The above value of σ for *Pt*-Ni alloys will be used later in order to evaluate the theoretical prediction regarding a T^3 term in the electronic specific heat.)

The work of Engelsberg *et al.* also predicts low-temperature electronic specific-heat terms having both T^3 and $T^3 \ln T$ dependences. The latter term (for the alloys) is shown[7] to be simply $3c/2\eta$ times the corresponding term for the pure host matrix. (η is the localized enhancement parameter and is explicitly defined below.) Since a $T^3 \ln T$ term is neither expected nor observed in pure Pt, and since $3c/2\eta$ is only ~ 1 for a *Pt*-6% Ni alloy for example, it follows that no $T^3 \ln T$ term is expected to be observed in dilute *Pt*-Ni alloys in the liquid-helium temperature range nor is such a term found experimentally.

In regard to the predicted T^3 term, however, it may be recalled that the present experimental results do show a significant variation with composition of the coefficient of the T^3 term in the total specific heat. But a change of some magnitude in the T^3 (lattice) specific-heat term is to be expected simply because of the addition of impurity atoms to a host matrix, and it is therefore appropriate to obtain, at this point, a rough estimate of the sign and the likely order of magnitude of such an effect. The desired estimate may be obtained from calculations[25] which consider the change in the lattice specific heat due to the introduction of an isotopic, substitutional impurity atom. In this case, which may yield a crude estimate of the effect for an alloy composed of the isoelectronic Pt and Ni atoms, the change in the coefficient of the T^3 specific-heat term is given by $(1/\beta')(d\beta'/dc) \cong -\frac{3}{2}\epsilon$, where $(1-\epsilon)$ is the ratio of the atomic weight of an impurity atom to that of a matrix atom. For Pt-Ni alloys, $\epsilon = 0.70$ and $(1/\beta') \times (d\beta'/dc) \simeq -1$, whereas the experimental data yield $(1/\beta')(d\beta'/dc) \sim -3$ to -7. It therefore appears that the observed changes in the T^3 term are not due simply to lattice-impurity effects; it is then appropriate to consider the detailed predictions of the local-enhancement theory.

The local-enhancement theory (for the case of significant host enhancement), as applied by Engelsberg *et al.*,[7] yields the following prediction for the coefficient $\Delta\beta'$ of the spin-fluctuation-related T^3 term in the electronic specific heat:

$$\Delta\beta' = -\frac{27\pi^4}{40} \times \frac{\gamma(\text{host})}{(m^*/m)_{\text{host}}} \times \frac{n_e^2(1/\eta)^3}{T_F^2 \times (\kappa_0^2 + \frac{1}{3}\bar{I}\sigma)^3} \times c,$$

where γ, m^*/m, κ_0^2, $\bar{I}$, σ, and c have been defined previously; n_e is the number of electrons per atom; T_F is the Fermi temperature for the host; and $1/\eta$ is the localized enhancement parameter, defined by $1/\eta \equiv [1/\chi(\text{host})][d\chi(\text{alloy})/dc]$. The magnitude of the predicted effect under discussion may conveniently be expressed as follows:

$$\left\{\left[\frac{1}{\beta'(\text{Pt})}\right]\left[\frac{d\beta'(\text{alloy})}{dc}\right]\right\}_{\text{SF}} = \frac{\Delta\beta'}{\beta'(\text{Pt}) \times c} \simeq -5 \times 10^{-4},$$

where the subscript SF again indicates the spin-fluctuation contribution, and where previously mentioned values have been used for the various parameters, along with[26] $\gamma(\text{Pt}) \simeq 6.5$ mJ/mole deg^2, $\beta'(\text{Pt}) \simeq 0.15$ mJ/mole deg^4, $T_F(\text{Pt}) \simeq 10^5$ °K, and $n_e = 10$. It should be specifically noted—and this is true not only for the present paper but for the paper[7] dealing with *Pd*-Ni alloys as well—that the T^3 specific-heat contribution under discussion is numerically evaluated by using, in addition to other parameters, a value for σ which is explicitly *chosen* to yield agreement between the change in the linear (γT) term observed experimentally and the change calculated theoretically from the theory under discussion. Since the predicted T^3 contribution is far smaller than the observed effect (in both *Pd*-Ni and *Pt*-Ni alloys), it seems reasonable to conclude, in the light of the previous discussion, that neither the change in the linear term nor the change in the T^3 term observed experimentally is adequately accounted for by the local-enhancement theory, even in the presence of exchange enhancement in the host matrix and with the introduction of a host-interaction range parameter.

An alternative treatment of local spin-fluctuation enhancement effects in an exchange-enhanced host matrix containing dilute impurities has been given by Chouteau *et al.*,[8] as was mentioned very briefly above; some of the details of their work will now be considered.

The basic formula which the above authors quote for the predicted changes in the low-temperature electronic specific heat has precisely the same functional dependence upon temperature as the results of Engelsberg *et al.*, although the two treatments differ significantly not only in regard to certain analytical details but also in regard to the nature and intended use of the parameters which occur.

Thus, Chouteau *et al.*, write, for the extra specific heat per impurity,

$$\frac{\Delta C_v}{T} \approx \Delta\gamma_0 \left(1 + \frac{6\pi^2}{5} \frac{\alpha_0(\alpha_0 - 1)}{\lambda} \times \frac{T^2}{T_{f(0)}{}^2} \ln \frac{T}{T_{f(0)}} - \frac{4\pi^2}{5} \frac{T^2}{T_{f,\text{loc}}{}^2}\right);$$

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[24] A. M. Clogston, Phys. Rev. Letters **19**, 583 (1967).

[25] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

[26] Sources of data for γ and β' of pure Pt include D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) **257**, 250 (1960); M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, *ibid.* **A285**, 561 (1965); K. G. Ramanathan and T. M. Srinivasan, Proc. Indian Acad. Sci. **A49**, 55 (1959). The value of T_F(Pt) was obtained from the Fermi energy given in Ref. 22.

the various parameters are defined (by Chouteau *et al.*) in terms of local and host-matrix interactions as well as the host-matrix dynamic susceptibility, although these authors do not employ the definitions to evaluate $T_{f,\text{loc}}$, $T_{f(0)}$, etc., from more basic parameters. Rather, they use experimental data, along with the above equation, to calculate values of the two "characteristic temperatures" just listed. Thus, for *Pd*-Ni alloys, and within the framework of the above equation, they use experimental data on changes in the linear and T^3 terms in the specific heat to calculate that $T_{f,\text{loc}}(Pd\text{-Ni}) \simeq 20 \pm 4°\text{K}$.

A similar procedure may be followed for *Pt*-Ni alloys, in which case the present experimental results, when interpreted in terms of the above equation, yield $T_{f,\text{loc}}(Pt\text{-Ni}) \sim 12\text{–}20°\text{K}$, if no lattice-defect term in the specific heat is included, or $\sim 13\text{–}25°\text{K}$, if the previously mentioned crude approximation to a lattice-defect term is included. [The range of values obtained in each case follows from the use of $(1/\beta')(d\beta'/dc) \sim -3$ to -7.] Since the $T_{f,\text{loc}}$ parameter involves, in principle, not only the properties of the host matrix (via its dynamic susceptibility function) but also the properties of the impurity atom (via a parameter which measures the increase in the exchange interaction in the neighborhood of the impurity), it is consequently difficult to assess, on the basis of currently available information, the significance of the approximate equality of $T_{f,\text{loc}}$ for dilute *Pd*-Ni and *Pt*-Ni alloys.

Electrical Resistivity

The effect of strong local-exchange enhancement upon the low-temperature electrical resistivity of dilute strongly paramagnetic transition-metal alloys was also first considered by Lederer and Mills.[4] They calculated the resistivity contribution due to the scattering of s electrons by spin-density fluctuations in the d band for the case of a single impurity atom in a matrix with significant enhancement. If the intra-atomic repulsion between d electrons is especially large in the immediate vicinity of the impurity atom—which seems to be a reasonable assumption for Ni impurities in Pd and Pt—then the d-band spin-density fluctuations will be especially large around the impurity atom and strong scattering of the s electrons will occur. The theory of Lederer and Mills predicts a spin-fluctuation-related resistivity contribution which is proportional to the square of the absolute temperature, as would be expected for any electron-electron scattering process. For sufficiently dilute alloys (i.e., for noninteracting impurity atoms) this effect varies linearly with the concentration of the dilute impurity. The proportionality coefficient A of this T^2 term is predicted[4] to depend upon impurity concentration c as follows:

$$A(c) = A_0[1 + \Gamma\alpha^2(\delta U/U_0)^2 c],$$

where A_0 refers to the host matrix; U_0 is a measure of the strength of the electron-electron interaction in the host, and $(U_0 + \delta U)$ is the corresponding quantity within a cell containing an impurity atom; Γ is a parameter which may be approximated[27] in the present case as $\approx \frac{1}{6} n_d \alpha_0^2$ (where n_d is the number of d-band holes and α_0 is the exchange-enhancement parameter in the host); and, finally, α is a parameter which is most directly expressed in terms of the real part of the frequency and wave-number-dependent dynamic susceptibility function for the host, i.e., $\alpha^{-1} = 1 - \delta U \times \sum_q \chi_R(q,0)$.

In order to compare the above theoretically derived relationship for $A(c)$ with experiment, it is necessary to obtain reasonable estimates for the values of the various parameters involved. Since $n_d(\text{Pt})$ [28,29] $\simeq 0.4$ holes/atom and $\alpha_0(\text{Pt})$ [22] $\simeq 5/3$, the value of Γ is $\sim \frac{1}{5}$. An estimate of the entire factor $\alpha(\delta U/U_0)$ may be obtained from magnetic susceptibility data, since a straightforward application of the theory under discussion yields[4] the following relation for the concentration dependence of the magnetic susceptibility:

$$(1/\chi)(d\chi/dc) = \alpha(\delta U/U_0)[U_0\chi(0)],$$

where $\chi(0)$ refers to the host matrix. Since experimental data for dilute *Pt*-Ni alloys and for pure Pt yield[22,23] $(1/\chi)(d\chi/dc) \simeq 10\frac{1}{2}\text{–}12$ and $U_0\chi(0) = \alpha_0 - 1 = \frac{2}{3}$, the second relationship above gives $\alpha(\delta U/U_0) \simeq 15\text{–}18$.

Substitution of these estimates of Γ and $\alpha(\delta U/U_0)$ into the relationship involving $A(c)$ then gives the theoretical prediction that

$$[A(c)]_{\text{SF}} \simeq [A(\text{Pt})]_{\text{SF}} \times [1 + 55c]$$

or

$$(A^{-1}dA/dc)_{\text{SF}} \simeq 55,$$

where the subscript SF serves to emphasize that this relation concerns only the spin-fluctuation contribution. The experimental results, on the other hand, may be expressed as

$$[A(c)]_{\text{expt}} \simeq [A(\text{Pt})]_{\text{expt}} \times (1 + 28c)$$

or

$$(A^{-1}dA/dc)_{\text{expt}} \simeq 28,$$

in which case it should be emphasized that the measured value of the T^2 term in the low-temperature electrical resistivity will have included all types of

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[27] The explicit form of Γ is given in Ref. 4, wherein the presently used approximation is suggested and discussed. (In order to avoid confusion with the specific-heat parameter, the present paper uses "Γ" to designated that combination of quantities which Ref. 4 designates as "γ.") The numerical factor of $\approx \frac{1}{6}$ used in the present paper is based essentially on a rough estimate of the diameter of the cylindrical d-hole surfaces in Pt (see Ref. 29) and differs only slightly from the factor of $\sim \frac{1}{4}$ which was estimated for Pd by Lederer and Mills (Ref. 4).

[28] A rough estimate of $n_d(\text{Pt})$ was obtained from the size of the Γ-centered, closed electron surface in Pt [see Ref. 29 and, also, L. R. Windmiller, J. B. Ketterson, and S. Hornfeldt, Jr., J. Appl. Phys. (unpublished)].

[29] L. R. Windmiller and J. B. Ketterson, Phys. Rev. Letters **20**, 324 (1968).

electron-electron scattering—including those which do not result in spin flips.

Two conclusions may finally be drawn regarding the extent of agreement between theory and experiment for the resistivity. On the one hand, the semiquantitative agreement between the above theoretical and experimental expressions for $A(c)$ would suggest that the spin-fluctuation contribution to the low-temperature electrical resistivity of dilute *Pt*-Ni alloys is certainly significant and perhaps dominant. On the other hand, the factor-of-2 difference between the theoretical and experimental values for $(1/A)(dA/dc)$ may be viewed as at least qualitatively significant. In this case, the theory and experiment taken together are consistent with the presence of an additional, concentration-independent contribution to the resistivity having the form $A'T^2$, where $A'\sim\frac{1}{2}[A(\text{Pt})]_{\text{expt}}$. A term of this type and magnitude might well arise from non-spin-flip (Baber) electron-electron scattering.

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Electronic States in Liquid Metals: A Generalization of the Coherent-Potential Approximation for a System with Short-Range Order*

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The problem of finding the ensemble averaged Green's function $\langle G\rangle$ which describes an electron moving in the potential field of N stationary scatterers is formulated in terms of multiple scattering theory. The correlations between the positions of the scatterers are explicitly taken into account. By making use of the quasicrystalline approximation and a generalization of the coherent-potential prescription, a procedure for calculating $\langle G\rangle$ is proposed. Because of the use of the quasicrystalline approximation, it involves only the radial distribution function of the scatterers in addition to the scatterer-electron interaction potential. It is shown that the procedure reduces to the coherent-potential approximation for randomly distributed scatterers, i.e., no short-range order, and to Korringa's band-structure calculation for an order lattice. It is pointed out that the method is applicable to the problem of electronic states in random alloys and that of vibrational spectra of imperfect crystals.

I. INTRODUCTION

When a metal is in the crystalline state the motion of its conduction electrons is reasonably well understood in comparison with what is known about their behavior after the crystal melts. The main reason for this difference is that in the former case the single-particle energy eigenfunctions depend on the coordinates of all the ions only in a relatively simple manner due to the Bloch condition. Since the structure is periodic it is sufficient to solve the Schrödinger equation for only a single unit cell. The situation in a liquid metal is much more complicated. The single-particle energy eigenstates then depend on all the ionic coordinates in an intricate fashion, and all the static correlation functions that are necessary to describe the liquid state in complete detail will enter into the problem.

The difficulty caused by the lack of translational symmetry manifests itself right at the outset of a calculation. In the crystalline state, the free-electron model with an effective mass serves as a reasonable starting point for perturbation theory in spite of the fact that the interaction between electrons and ions is not small. In the liquid state, the wave vector is not a good quantum number and hence the effective-mass approximation does not help. In principle, one is faced with infinite order perturbation theory right from the beginning. In fact it was an important advance, and gave much impetus to current work on electrons in liquid metals when Ziman[1] showed that one may start from free electrons and use perturbation theory provided the ions replaced by a suitably defined pseudo atoms whose interaction with the electrons is small and therefore can be treated in low-order perturbation theory.

A more fundamental approach to the problem has been provided by Edwards.[2,3] He considered the dynamics of an electron moving in the potential field of N

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[1] J. M. Ziman, Phil. Mag. 6, 1013 (1961).

[2] S. F. Edwards, Phil. Mag. 3, 1021 (1958).

[3] S. F. Edwards, Phil. Mag. 6, 617 (1961).