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Effect of Pressure on the Low-Temperature Electrical Resistance of Pure Pd and Very Dilute Pd : Ni Alloys*†

R. A. Beyerlein‡ and D. Lazarus
Department of Physics and Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801

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Measurements of the low-temperature electrical resistivity of pure Pd and a series of very dilute Pd:Ni alloys (0.32-, 0.55-, and 1.0-at.% Ni) have been carried out under hydrostatic pressure (~4.5 kbar) using solid helium as the pressure medium. It has been found that the coefficient of the T^2 contribution believed to arise from paramagnon-enhanced electron-electron scattering is reduced upon application of pressure for each alloy by an amount greater than that estimated on the basis of a localized-exchange-enhancement model coupled with earlier magnetostriction work. The dependence of this effect on the concentration of Ni is compared with the prediction of a localized-exchange-enhancement model. The results are consistent with the idea that electron-paramagnon scattering gives rise to a negative deviation from T^2 behavior—of order greater than T^2 and less than T^5—in the alloys which is more strongly reduced in size upon application of pressure than is the T^2 contribution itself. For the alloy containing 1-at.% Ni both the zero-pressure data and the pressure data indicate that a description of the temperature-dependent resistivity $\rho(T)$ for $T < 10\,^\circ\mathrm{K}$ by $\rho = \rho_0 + AT^2 + BT^5$, as has previously been suggested, is inadequate. A large reversible decrease in the residual resistivity of each of the alloys was observed upon application of pressure. The relative size of this effect is four times as large as the relative volume change. This suggests that there may be a significant transfer of low-mobility *d* electrons to high-mobility *s* states with application of pressure. A simple model is offered to explain the role of Ni in this effect.

I. INTRODUCTION

A. Review of Exchange Enhancement

A single Ni atom dissolved in a Pd host does not give rise to a local moment even at 0 °K, but the presence of the Ni significantly increases the polarizability of the Pd host in the vicinity.[1] Such a system is known as an "exchange-enhanced" alloy and, along with similar systems, it has been intensively studied with a view towards understanding the onset of the magnetic state. The Pd : Ni system is a particularly appropriate testing ground for specific models of exchange enhancement since Pd and Ni are isoelectronic and the Hartree–Fock impurity potential should be negligibly small. Our data show that the residual resistivity of the alloy with 1-at.% Ni is only 0.3 $\mu\Omega$ cm larger than the value for pure Pd, and so this approximation seems reasonable.

The dominant feature of the existing models of exchange enhancement is the way in which the intra-atomic (*d* band) Coulomb repulsion terms are included. As a starting point the limit of the screened Coulomb interaction is approximated by the "Stoner-model" limit of a repulsive δ-function interaction. In the subsequent Hartree–Fock calculation the tendency towards spin ordering through exchange interactions corresponds to removing the Coulomb interaction corresponding to antiparallel configurations from the energy of the system. The ratio of the uniform susceptibility of the exchange-enhanced system, χ, to the susceptibility in the Hartree picture (without exchange), χ^0, is called the Stoner enhancement factor S. For Pd,

$$\frac{\chi_{\mathrm{Pd}}}{\chi^0_{\mathrm{Pd}}} = \frac{1}{1 - U_0 N(0)} = S\,. \qquad (1)$$

Here χ^0_{Pd} is the susceptibility per Pd atom in the Hartree picture (without exchange), U_0 is the size of the intra-atomic Coulomb repulsion between a pair of electrons in the *d* band, and $N(0)$ is the bare band density of states of electrons in the *d* band at the Fermi energy.

A localized-exchange-enhancement model (LEEM) in which a single Ni impurity serves to increase the *local* exchange field seen by the *d* electrons affords a fairly good description of the Pd : Ni alloys. Lederer and Mills[2] formulated such a model in the single-impurity limit and applied it to the calculation of the magnetic susceptibility and the T^2 contribution to the electrical resistivity of the alloys. Their result for the enhanced susceptibility for a concentration c of impurities is

$$\frac{\chi(c)}{\chi_{\mathrm{Pd}}} = 1 + c\;\Delta I_{\mathrm{eff}}\,\chi_{\mathrm{Pd}}\,, \qquad (2)$$

where

$$\Delta I_{\mathrm{eff}} = \frac{\delta U}{1 - \delta U \bar{\chi}(\omega)}$$

and (3)

$$\bar{\chi}(\omega) = \frac{1}{N}\sum_k \chi_0(k,\omega)\,.$$

Here the intra-atomic Coulomb repulsion term U_I associated with the Ni impurity is assumed to be larger than the corresponding term U_0 for the matrix by the amount $\delta U = U_I - U_0$. $\chi_0(k, \omega)$ is the susceptibility per atom of the matrix under the influence of a small magnetic field of wave vector k and amplitude H_k. χ_{Pd} is the dynamical susceptibility $\chi_{\text{Pd}}(k, \omega)$ of the host with exchange enhancement; thus the statement that the dilute alloy contains long-wavelength low-frequency spin fluctuations (paramagnons) is contained in Eq. (2). The paramagnon energy spectrum follows from the low-frequency poles of the susceptibility function given in Eq. (2). This furnishes a starting point from which to calculate the influence of paramagnons on other low-temperature properties of the dilute-alloy system.

Englesberg, Brinkman, and Doniach[3] have reevaluated the single-impurity limit of the LEEM and extended it to a many-impurity limit for the calculation of the specific heat. Their expression for the susceptibility of the dilute-alloy system is

$$\frac{\chi(c)}{\chi_{\text{Pd}}} = \frac{1}{1 - c\,\Delta I_{\text{eff}}\,\chi_{\text{Pd}}} , \qquad (4)$$

where ΔI_{eff} is of the same form as given in Eq. (3).

The role of spin fluctuations (paramagnons), which are expected to appear in all exchange-enhanced systems, has been of particular interest throughout the intensive investigation of the Pd-Ni system in recent years.[4-8] Detailed studies of the electronic structure of pure Pd through de Haas–van Alphen measurements[9,10] and theoretical band-structure calculations[11] cast doubt on the applicability of an exchange-enhancement model in explaining the incipient ferromagnetic behavior of Pd itself. In particular, the paramagnon enhancement of the band-structure effective mass, as deduced from the specific-heat measurements,[5,6,12] is perhaps an order of magnitude smaller than the predictions of the current models of exchange enhancement.[13] On the other hand, these models account fairly well for the effect of alloying on the magnetic susceptibility, the specific heat, and the electrical and thermal resistivities.

B. Pressure Dependence of the Low-Temperature Electrical Resistivity of Pd:Ni

There is little information available on the volume dependence of the low-temperature properties of any of the above systems, and prior to the work of Fawcett *et al.*,[14] none on dilute solutions of Ni in Pd.[15] The existing models of exchange enhancement may be applied to predict the volume dependence of the low-temperature properties of dilute Pd : Ni alloys as a function of concentration of Ni. The magnetostriction measurements[14] coupled with the many-impurity limit of the LEEM yield an estimate of the volume dependence of the "effective impurity potential" [Eq. (3)] as well as the volume dependence of the intra-atomic Coulomb repulsion term U_0 for pure Pd, thus furnishing the necessary information to estimate the volume dependence of other low-temperature properties of the dilute Pd : Ni system. The effect of hydrostatic pressure on the low-temperature electrical resistivity and/or the magnetic susceptibility of Pd : Ni would therefore provide an important additional check on the validity of the current formulations of the LEEM.

In its current formulation the LEEM predicts only a T^2 contribution from electron-paramagnon scattering to the low-temperature electrical resistance over the range of the present measurement. Kaiser and Doniach[8] show that the Bose character of the localized paramagnons leads to a gradual change in the temperature dependence of the spin-fluctuation resistivity from T^2 to T at sufficiently high temperatures (above about 19 °K in the case of Pd : Ni). Schindler and Rice[4] suggested the presence of a "negative T^5" contribution due to electron-paramagnon scattering in order to explain their observation that the T^5 contribution normally associated with electron-phonon scattering decreased with increasing Ni concentration, becoming negative for Ni concentrations exceeding about 0.5 at.%. In the framework of the exchange-enhancement models, it seems clear that a contribution ($B_n T^n$) to the electrical resistivity of higher order than T^2 associated with electron-paramagnon scattering would be more sensitive to a change in volume than the large T^2 contribution attributed to spin fluctuations in Pd : Ni. Thus a measurement of the low-temperature electrical resistivity of a series of alloys under hydrostatic pressure should provide evidence whether the negative deviation from T^2 behavior observed by Schindler and Rice[4] is indeed associated with electron-paramagnon scattering.

We have undertaken to measure the pressure dependence of the low-temperature electrical resistivity of pure Pd and of Pd : Ni alloys of composition 0.32-, 0.55-, and 1.0-at.% Ni in the temperature range 2–12.3 °K using hydrostatic pressures (solid helium) up to 4.5 kbar.

Since the T^2 contribution to the low-temperature electrical resistivity is well based in paramagnon theory, it is of particular importance to estimate the effect of pressure on the coefficient $A(c)$ of this contribution. We present below an estimate of this effect for pure Pd and for dilute Pd : Ni alloys.

For pure Pd the LEEM reduces to the uniform-exchange-enhancement model (UEEM), in which the size of the intra-atomic Coulomb repulsion between a pair of electrons in the d band (U_0) becomes the relevant parameter. Schindler and Rice's[4] original calculation of $A(0)$ was done in an approximation which neglected the k dependence of the dynamical susceptibility.[16] Mathon[17] has repeated the calculation including the k dependence. His result, neglecting numerical factors and physical constants, is

$$A(0) \sim \frac{J^2 m_s^2 m_d}{n_s^2} \frac{k_d^2 N(0)}{[U_0 N(0)]^{3/2}[1-U_0 N(0)]^{1/2}} ,$$

where J is an s-d exchange parameter, m_s and m_d are, respectively, the effective mass of an s and a d electron, n_s is the number of s electrons per unit volume, k_d is the d-electron Fermi wave vector, $N(0)$ is the density of states at the Fermi level, and U_0 is the intra-atomic Coulomb repulsion between a pair of electrons in the d band.

The volume dependence of J, m_s, and m_d are assumed to be negligible. We neglect the possibility of any significant s to d transfer with small changes in volume. Although this approximation may be unrealistic, it will not affect the general form of the volume dependence of $A(c)$ as a function of concentration, which is calculated later. Thus,

$$\frac{\partial \ln A(0)}{\partial \ln V} = -2\frac{\partial \ln n_s}{\partial \ln V} + 2\frac{\partial \ln k_d}{\partial \ln V} - \frac{1}{2}\frac{\partial \ln N(0)}{\partial \ln V} - \frac{3}{2}\frac{\partial \ln U_0}{\partial \ln V} + \frac{1}{2}\frac{\partial \ln S}{\partial \ln V} , \quad (5)$$

where S is the Stoner enhancement factor [Eq. (1)]. The volume derivative of the density of states is taken to be 1.5, a typical value for transition metals without pronounced exchange enhancement.[18] From magnetostriction measurements of Fawcett *et al.*[14]

$$\frac{\partial \ln \chi_{\mathrm{Pd}}}{\partial \ln V} \approx -3.5 .$$

Using these values and taking $S = 10$, it is deduced that

$$\frac{\partial \ln U_0}{\partial \ln V} = -2 .$$

From Eq. (1),

$$\frac{\partial \ln S}{\partial \ln V} = \frac{\partial \ln \chi_{\mathrm{Pd}}}{\partial \ln V} - \frac{\partial \ln N(0)}{\partial \ln V} ,$$

and, substituting the values given above,

$$\frac{\partial \ln S}{\partial \ln V} = -5 .$$

Neglecting s to d transfer implies that

$$\frac{\partial \ln n_s}{\partial \ln V} = -1 ,$$

and this approximation also makes reasonable a crude estimate of the volume dependence of k_d on the basis of free-electron theory, $k_d \sim V^{-1/3}$. Then Eq. (5) becomes

$$\frac{\partial \ln A(0)}{\partial \ln V} \approx 1 .$$

Alternatively,

$$\frac{1}{A(0)} \frac{\partial A(0)}{\partial p} \approx -\kappa , \quad (6)$$

where p is the pressure and the compressibility κ is defined by

$$-dV/V = \kappa\, dp .$$

Proceeding to the calculation for the alloys, we make use of the result of Lederer and Mills[2] for the coefficient of the T^2 contribution to the electrical resistivity,

$$\frac{A(c)}{A(0)} = 1 + \left(\frac{\Delta I_{\mathrm{eff}}}{U_0}\right)^2 \gamma c , \quad (7)$$

where, neglecting numerical factors and physical constants,

$$\gamma \sim a \frac{\epsilon_s}{v_s} n_s V \frac{\beta_I}{\beta} S^2 . \quad (8)$$

Here a is the lattice constant for the fcc Pd : Ni system, ϵ_s is the Fermi energy for s electrons, v_s is the corresponding Fermi velocity, n_s is the number of s electrons per unit volume, V is the volume of the system, S is the Stoner enhancement factor, and β_I/β is the ratio of two dimensionless definite integrals. β_I/β^2 is not expected to depend significantly on volume in our approximation of neglecting s to d transfer. Then the volume dependence of $A(c)$ is given by

$$\frac{\partial \ln A(c)}{\partial \ln V} - \frac{\partial \ln A(0)}{\partial \ln V} = \frac{A(c)-A(0)}{A(c)} \times \left(2\frac{\partial \ln \Delta I_{\mathrm{eff}}}{\partial \ln V} - 2\frac{\partial \ln U_0}{\partial \ln V} + \frac{\partial \ln \gamma}{\partial \ln V}\right) . \quad (9)$$

In order to compute the volume derivative of γ [Eq. (8)] note that $V n_s$ as defined above does not change in the approximation that s to d transfer is negligible. On the basis of free-electron theory $\epsilon_s/v_s \sim V^{-1/3}$, and since $a \sim V^{1/3}$, the volume dependence of γ is contained solely in the factor S^2. Fawcett *et al.*[14] deduce that $\partial \ln \Delta I_{\mathrm{eff}}/\partial \ln V \approx 7.5$.

Then Eq. (9) becomes

$$\frac{\partial \ln A(c)}{\partial \ln V} - \frac{\partial \ln A(0)}{\partial \ln V} = \frac{A(c)-A(0)}{A(c)} \times 2\left(\frac{\partial \ln \Delta I_{\mathrm{eff}}}{\partial \ln V} - \frac{\partial \ln U_0}{\partial \ln V} + \frac{\partial \ln S}{\partial \ln V}\right) \approx \frac{A(c)-A(0)}{A(c)} \times 9$$

or, alternatively,

$$\frac{1}{A(c)}\frac{\partial A(c)}{\partial p}-\frac{1}{A(0)}\frac{\partial A(0)}{\partial p}\approx-\kappa\,\frac{A(c)-A(0)}{A(c)}\times 9 \quad . \quad (10)$$

In order to estimate the size of the pressure effect we take for pure Pd $\kappa \sim 0.5\times10^{-6}$ bar^{-1}.[19] Then for a pressure of 5 kbar the estimate for pure Pd is, from Eq. (6),

$$\Delta A(0)/A(0)\approx-2.5\times10^{-3} \ .$$

This decrease in resistance with pressure is too small to be detected in this experiment.

For an alloy containing 1-at.% Ni, $A(c)\approx 9A(0)$.[7] Then for a pressure of 5 kbar the relative change in $A(c)$ is, from Eq. (10),

$$\Delta A(c)/A(c)\approx-2.2\times10^{-2} \ .$$

In other words, a pressure of 5 kbar should result in about a 2% decrease of the coefficient of the T^2 contribution for a 1-at.% alloy. An effect of this order of magnitude should be well above the limits of resolution of our measurement. Finally, note that from Eq. (10) the relative change in $A(c)$ with the application of 5 kbar of pressure will be less than the above value for concentrations of Ni less than 1 at.%.

If there is present in the low-temperature resistivity a contribution from electron-paramagnon scattering of order higher than T^2, then it seems reasonable that the sign of the associated pressure effect should be the same as above. As suggested earlier, the relative size of this effect could be significantly larger than the corresponding pressure effect estimated above for the T^2 term.

The above description of the Pd : Ni system in terms of a LEEM assumes a homogeneous alloy. Except in the case of the most dilute alloys, one cannot discount the possibility of chemical clustering on a microscopic basis. A model for the influence of clustering might be extremely valuable in interpreting the pressure effects which are not expected to be complicated by a change in the amount of clustering with pressure.

II. EXPERIMENTAL METHOD

A. Sample Preparation

Samples were prepared using a "cold-crucible" method in a purified Ar atmosphere, applying power by induction. The cold crucible consisted of a Ag-tube "cradle" fashioned from a continuous tube on which the sample was supported.[20] This assembly was placed inside an induction coil under a bell jar. The crucible was cooled by a continuous flow of cooling water through the tube.[21]

Samples were prepared from pure-Pd sponge (99.9995% nominal purity) supplied by Johnson-Mathey and solid Ni (99.999% nominal purity) supplied by United Mineral and Chemical Co. A master alloy (8-at.% Ni) was prepared prior to the preparation of the dilute-alloy samples. Each sample (~ 1 g) was turned over at least four times during the course of the melt in order to ensure sample homogeneity.

The melted samples were cold worked into cylinders of about 0.105-in. diameter prior to swaging into wires. The 0.55- and the 1.0-at.%-Ni samples were reduced to 0.0255-in. diameter; the pure-Pd samples and the 0.3-at.%-Ni samples were further reduced to 0.020-in. diameter. At various stages during the cold working and swaging operation each sample was etched, sealed in vacuum in quartz, and annealed. The etchant was a mildly heated solution of one part nitric acid and one part water. Several drops of hydrogen peroxide were added just before use. After the final swaging pass the samples were again etched and annealed for 24 h at 1050 °C.

The analyses of the final wire samples are presented in Table I.

B. Pressure Vessel

The pressure vessel (Fig. 1) for the low-temperature resistance measurements was machined from Berylco 25 and subsequently heat treated for 3 h at 610 °F. The vessel includes a port external to the pressurized region for mounting the control sample or "dummy" and various tapped-screw holes used for mounting thermometers and electrical grounds. The vessel was designed to work at pressures as high as 10 kbar.

The four electrical leads for a conventional

TABLE I. Analysis of wire samples.

Conc.[a] of Ni (at. %)	Compositional[b] uniformity over 20-μin. resolution (at. %)	Fe content[c] (ppm, atomic)	Other trace[c] impurities (ppm, atomic)
(Pure Pd)		4	Pt 1.5; W 0.6; Ag 3; Nb 2; Ti 1
0.323 ± 0.007 (0.32)		38	Pt 0.7; W 0.4; Ag 35; Nb 3.5; Cu 9.5; Ti 2.7
0.554 ± 0.006 (0.55)		4	Pt 1.5; W 0.6; Nb 2; Cu 19; Ti 1
0.991 ± 0.011 (1.0)	0.06	16	Pt 1.6; Nb 3; Cu 38; Ti 4

[a] For all samples the values reported have been determined by wet chemical analysis. The number in parentheses for each alloy is the concentration value used in the text.

[b] From x-ray microprobe analysis (20 μin. = 20×10^{-6} in.).

[c] Mass spectrographic analysis; absolute analysis with a possible error of ± a factor of 3.

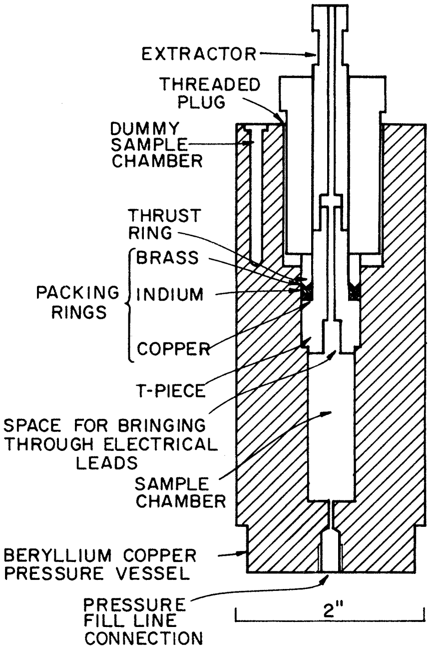

FIG. 1. Pressure vessel.

four-wire dc resistance measurement were introduced into the pressure cell via a length of four-conductor swaged tubing[22] which was brought through the Bridgman T piece (Fig. 2). The four-conductor swaged tubing was brazed to a $\frac{1}{4}$-in. stainless-steel collar which was in turn brazed to the Bridgman T piece. The final brazing operation was performed in vacuum and the T piece was quenched in water immediately upon completion of the brazing process. This elaborate precaution was necessary in order not to greatly degrade the ultimate mechanical properties of Berylco 25. Finally, the stainless-steel sheath of the swaged tubing was electrochemically etched away to expose the four leads and the T piece was heat treated in the usual way.

In order to complete the pressure seal for the electrical leads, a small amount of alumina packing was removed from the upper end of the swaged tubing (≈ 1 mm depth) using a fine needle. A small bead of expoxy[23] was then formed in this depression where the leads emerged and allowed to cure for 24 h. The stainless-steel collar and swaged tubing were inset into the Berylco T piece so that the Epoxy bead was actually down inside a $\frac{1}{4}$-in.-diameter cup in the head of the T piece. A mixture of raw Epoxy base and $1\text{-}\mu$ glass beads (no hardener) was packed into this cup and around the Epoxy bead. This cryogenic pressure seal had a mixed performance record. On the basis of its performance at room temperature, it was not possible to predict the success of a seal at low temperature. The initial success of a seal during a pressure test at liquid-nitrogen temperature did not always guarantee its success in a low-temperature experimental run.

C. Sample Mounting

The sample was well supported on the head of the Bridgman T piece as shown in Fig. 2. Connections for the four-wire measurements were accomplished by spot welding 0.005-in. Pd wires to the sample and to the Cu leads emerging from the swaged tubing fixed in the center of the T piece. The method for sample mounting shown in Fig. 2 allowed the sample little freedom for movement as the pressurized He froze around it. This feature, coupled with a slow cooling rate from above the freezing point of the He, was essential for the elimination of any increase in residual resistivity after a pressure cycle at low temperature.

The control sample ("dummy") was fixed to the pressure vessel as indicated in Fig. 1. Although various schemes were tried to ensure that the dummy was well grounded thermally to the pressure bomb, none were entirely successful.

D. Resistance-Measurement System

This experiment employed a conventional four-wire potentiometric method for resistance measurement. Currents of about 0.050 A were supplied to

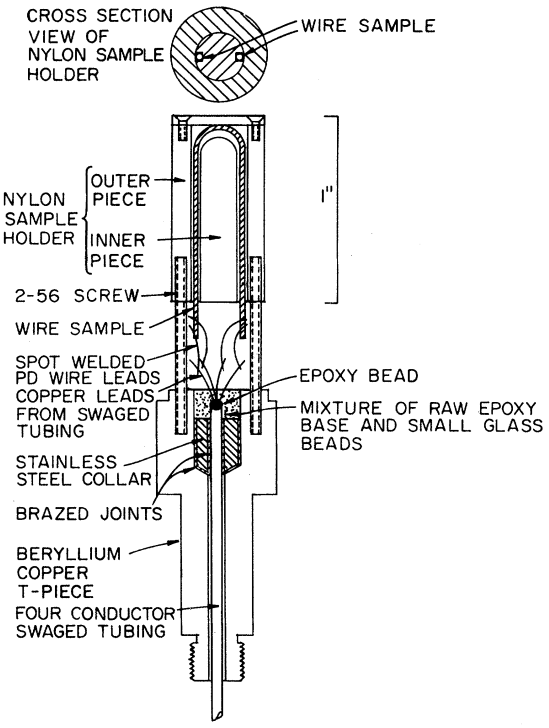

FIG. 2. Sample mounted on Bridgman T piece.

the sample and dummy by separate Willard DH-5-1 cells. After some initial tests this relatively low value for the work current was chosen in order to eliminate observable effects of Joule heating in the resistance measurements. This measuring current, as monitored by a Leeds & Northrup K-3 potentiometer, was stable to 2 or 3 parts in 10^5 in the course of a measurement.

The voltage drop across the sample and dummy was measured using a Honeywell model 2768 six-dial potentiometer and a Keithley model 148 nanovoltmeter as a null detector. The null detector was mounted on nylon screws and bushings and was used on battery operation. With these refinements it was possible to achieve a stability of ± 1.5 nV in most measurements.[24]

Voltage and current leads from the sample and dummy were brought out of the cryostat via Cu leads. All external connections were Cu to Cu and were either pressed contacts or joints made with thermal-free solder.

E. Cryogenic Apparatus

Low-temperature measurements were made using a conventional He^4 glass cryostat. The pressure bomb was enclosed in a brass vacuum can supported on two vacuum lines which also served as conduits for the pressure fill line and the electrical leads. Helium gas entered the pressure bomb via a $\frac{1}{32}$-in.-o.d.×0.008-in.-i.d. stainless-steel fill capillary.[25]

In order to minimize problems of thermometry and of temperature uniformity between dummy and sample all measurements above 3 °K were done without exchange-gas coupling between the bomb and the He bath. The bomb and fill line were permanently connected to the bath via a system of metal thermal links. The link from the fill line to the bath consisted of two annealed 0.016-in.-diam Au wires running from the underside of the vacuum chamber cover to a $\frac{1}{4}$-in.-diam brass collar fixed to the fill line just above the bomb. Its purpose was to serve as a heat shunt for heat coming down the capillary fill line from room temperature. A similar link made of four annealed Au wires coupled the bomb to the bath. Three wires of the link were connected at the bottom of the bomb and the remaining wire was fixed to the top.

F. Resistance-Measurement Procedure

In most cases a complete series of measurements over the temperature range 2–12.3 °K was performed at low pressure before doing a run at high pressure. During each measurement the temperature of the bomb as monitored by the calibrated Ge resistor was stabilized and continually recorded. The temperature-control system[26] was capable of control to better than 0.1 m °K below 5 °K and to a few millidegrees at temperatures as high as 10 °K. Since beryllium-copper alloys have rather poor thermal conductivity at low temperature, care was taken to keep the thermal gradients in the pressure bomb as small as possible. The power level supplied by the temperature controller to the bomb heater had to be kept quite small in order that it not affect the measurement. This necessitated a rather elaborate series of measures for rough temperature control.[21] It was possible to stabilize temperatures as high as 12 °K with about 10 mW of heater power to the bomb. Temperatures below 8 °K could be stabilized with less than 5 mW of heater power.

In order to make measurements in the range 2–3 °K it was necessary to introduce He exchange gas into the vacuum chamber surrounding the bomb. One measurement was always made at $T \approx T_\lambda$ (He^4) with "positive" exchange-gas coupling.

The He level was allowed to fall below the level of the pressure bomb in preparation for pressurization. The pressure was raised in successive stages. For each stage the sharp warming response of the pressure vessel was used as the indication that the warm He gas had actually entered it. After the maximum pressure—usually 5 kbar—was achieved the bomb was allowed to cool slowly below the freezing point, keeping the fill line open. A rough indication of the freezing point was observed in the abrupt slowing and near halt of the pressure drop on an external Heise gauge.[27] Once it was certain that the He in the bomb had frozen, the fill-line heater power was reduced and the bomb was allowed to continue a slow cool-down via the Au-wire links. The final pressure in the cell was estimated from the appropriate isochore of solid He.[28] Details of the pressurization apparatus are described elsewhere.[21]

Upon successful completion of pressurization and cool-down—no leaks from the pressure vessel at low temperature could be tolerated—a series of resistance measurements in the range 2–12.3 °K was carried out as described above. For one of the alloys (1-at.% Ni) measurements were made at an intermediate pressure to check the linearity of the effect of volume change. After a pressure run was completed, a reversal of the procedure described above was used to release the pressure. The bomb was then cooled down once again and measurements at a series of temperatures were made to check reproducibility with the earlier "zero-pressure" measurements.

III. RESULTS AND ANALYSIS

A. Three-Parameter Data Analysis

The electrical resistivities at lower temperatures are expected to obey an equation of the form

$$\rho = \rho_0 + AT^2 + BT^5 . \qquad (11)$$

Following Schriempf,[29] Eq. (11) is rewritten as

$$(\rho - \rho_0)/T^2 = A + BT^3 . \qquad (12)$$

The BT^3 term falls off quite rapidly with decreasing temperature. It was found that a fairly good approximation for ρ_0 could be obtained by fitting the lower-temperature data to

$$\rho = \rho_0 + AT^2 .$$

The value of ρ_0 thus obtained was used as a starting value in fitting the data for $2 < T < 12.3$ °K to Eq. (12); ρ_0 was then varied until the least-squares fit to Eq. (12) went through a minimum. The position of this minimum was sensitive to incremental changes in ρ_0 well beyond the experimental resolution.

The data were fitted in this manner, except that the resistance values for the pressure measurements were corrected for the reduction in sample dimensions due to hydrostatic pressure in computing the corresponding resistivities. The dummy sample was used as a sensitive thermometer in correcting the zero-pressure resistance measurements and the resistance measurements under pressure to a common temperature. This procedure was necessary to correct for certain systematic temperature errors.

B. Results

Figures 3–6 show plots of the electrical resistivity $\rho(T)$ vs T^2 for pure Pd and for each of the alloys measured. Each plot gives the results of the zero-pressure measurements and the measurements under pressure for a single sample. The plot for the alloy containing 1-at.% Ni includes results for an intermediate pressure. The solid lines show the best fit to Eq. (12) in each case.

Figures 7–10 show plots of $[\rho(T) - \rho_0]/T^2$ vs T^3 for each sample. The solid lines represent the best fit to Eq. (12) in each case.

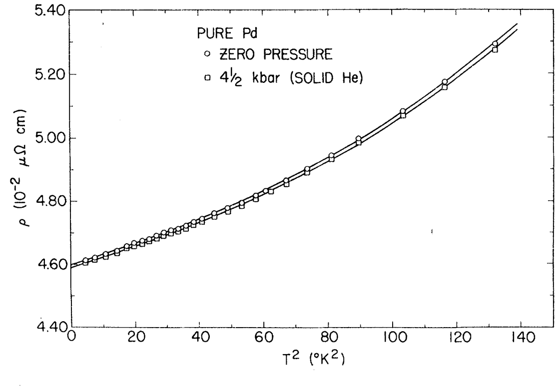

FIG. 3. $\rho(T)$ vs T^2 for pure Pd.

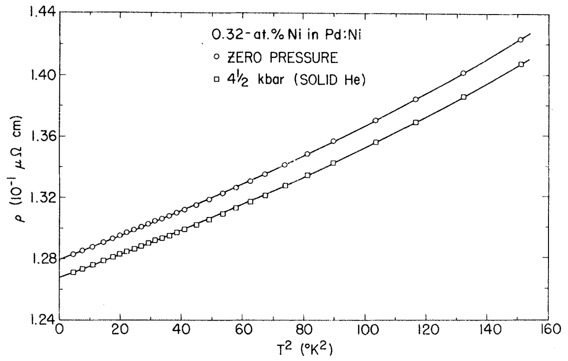

FIG. 4. $\rho(T)$ vs T^2 for the Pd : Ni alloy containing 0.32-at.% Ni.

A summary of results is given in Table II. $\Delta V/V$ is the relative volume change corresponding to the pressure at which the temperature run was made. To compute $\Delta V/V$ for each pressure we have used Bridgman's[30] value for the compressibility κ of Pd, presuming that κ does not change with slight Ni additions:

$$\kappa = \frac{1}{V_0}\frac{\partial V}{\partial p} = -a\times10^{-7} - 2b\times10^{-12}p ,$$

where the pressure p is given in kg/cm^2, $a = 5.28$, and $b = 2.1$. ρ_0, A, and B are, respectively, the residual resistivity, the coefficient of the T^2 term, and the coefficient of the T^5 term in the resistivity $\rho(T)$ [Eq. (11)]. Experimental uncertainties associated with these parameters are also given. The values for ρ_0 and A were found to be reproducible to well within the experimental error given in Table II. $\Delta\rho_0/\rho_0$ and $\Delta A/A$ are the relative changes in ρ_0 and A with pressure (with respect to zero-pressure values).

Table III summarizes the results of reannealing each sample after a low-temperature run and remeasuring the resistance at 4.2 °K. This proce-

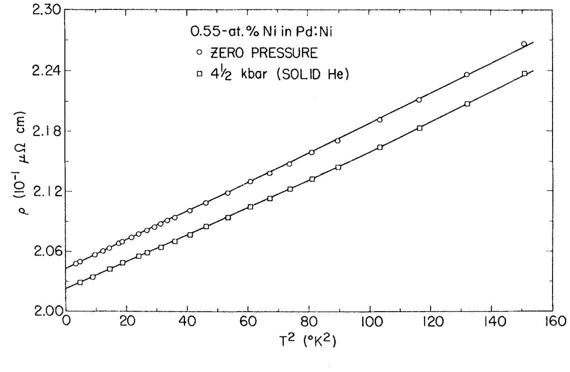

FIG. 5. $\rho(T)$ vs T^2 for the Pd : Ni alloy containing 0.55-at.% Ni.

TABLE II. Parameters of dilute Pd : Ni alloys—effect of pressure. The uncertainties given were computed from the known experimental precision. The corresponding uncertainties associated with the scatter of the measured resistivities from the best fit to Eq. (12) were always less. In the case of the parameters A and B the latter uncertainties were about $\frac{1}{3}$ as large as the uncertainties associated with the experimental precision for all cases except for the alloy containing 1-at.% Ni, where the fit of the measured resistivities to Eq. (12) was not good.

Ni conc. (at.%)	$\frac{\Delta V}{V}\times 100$ [a]	ρ_0 ($\mu\Omega$ cm)	$\frac{\Delta\rho_0}{\rho_0}\times 100$ [b]	$A\times 10^6$ ($\mu\Omega$ cm/°K^2)	$\frac{\Delta A}{A}\times 100$ [b]	$B\times 10^9$ ($\mu\Omega$ cm/°K^5)	Maximum temp. used in fit (°K)
(Pure Pd)	0	0.045 981 ± 0.000 023		33.0 ± 0.5		13.1 ± 2.0	11.49
	−0.239	0.045 896	−0.18[c]	32.5	−1.5	13.0	11.49
0.32	0	0.127 95 ± 0.000 03		78.6 ± 0.7		9.2 ± 1.2	12.28
	−0.243	0.126 78	−0.91[c]	75.9	−3.4	9.0	12.28
0.55	0	0.204 28 ± 0.000 04		143.4 ± 1.1		1.6 ± 2.0	12.28
	−0.243	0.202 29	−0.97	133.5	−6.9	3.9	12.28
1.0	0	0.335 83		248.7		−14.4	12.28
	−0.127	0.334 04 ± 0.000 06	−0.53	241.6 ± 1.6	−2.9[d]	± 2.4	6.00
	−0.239	0.332 35	−1.03	235.6	−5.3	−11.7	12.28

[a] $\Delta V/V$ is the relative volume change of each alloy corresponding to the pressure sustained by the solid helium at low temperature and computed from the compressibility given in Sec. III B.

[b] $\Delta\rho_0/\rho_0$ and $\Delta A/A$ are, respectively, the relative change in ρ_0 and A with the application of a pressure corresponding to the relative volume change $\Delta V/V$ shown in the second column.

[c] The pure-Pd sample and the alloy containing 0.32-at.% Ni suffered some cold work in mounting (see Sec. III B and Table III). The values of $\Delta\rho_0/\rho_0$ for the above alloy would presumably be about 12% higher for a well-annealed sample (Table III).

[d] The data in the upper part of the temperature range for the intermediate pressure run $[(\Delta V/V)\times 100 = -0.127]$ are incomplete. The parameters given are the results of the best fit to $\rho - BT^5 = \rho_0 + AT^2$ for the lower-temperature data where $\rho - BT^5$ is evaluated using the value for B obtained from the fit to the larger temperature range.

dure was used to check the amount of cold work which had been introduced into each sample as a result of mounting it in the sample holder for the low-temperature measurements under pressure. The effect is quite significant for the pure-Pd sample and is appreciable for the alloy containing 0.32-at.% Ni. Room-temperature resistivities are also given.

The main features of the resistivity data shown in Figs. 3–10 and summarized in Table II are: (i) The coefficient of the T^2 contribution (A) is reduced by the application of pressure in each case; (ii) the coefficient of the T^5 contribution (B) exhibits a rather complex dependence on pressure, depending on the concentration of Ni; and (iii) for each of the alloys, application of pressure results in a (reversible) decrease of the residual resistivity ρ_0.

Because the decrease in residual resistivity with the application of pressure was large and reversible, it was imperative that the pressure cell be absolutely tight for the period of two or three days necessary to complete the temperature run.

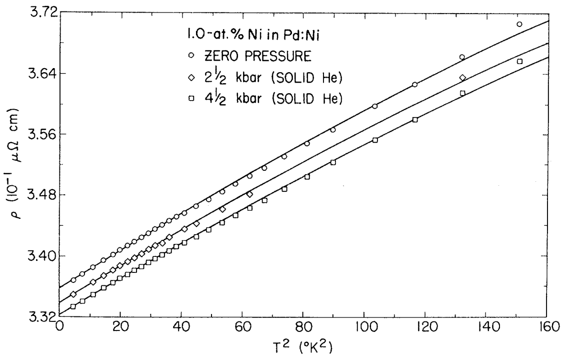

FIG. 6. $\rho(T)$ vs T^2 for the Pd : Ni alloy containing 1.0-at.% Ni.

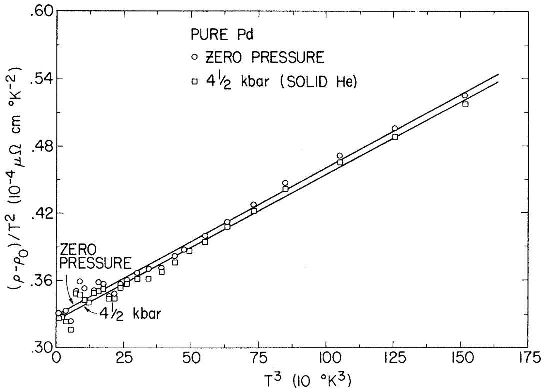

FIG. 7. $[\rho(T)-\rho_0]/T^2$ vs T^3 for pure Pd.

TABLE III. Room-temperature resistivity and resistivity at 4.2 °K after reannealing. Each sample was reannealed after each run and remeasured at 4.2 °K in order to check the amount of cold work which had been introduced during mounting for a low-temperature run with pressure.

Conc. of Ni (at.%)	Resistivity ($\mu\Omega$ cm) $T = 296$ °K	$T = 4.2$ °K	Recomputed ρ_0[a] ($\mu\Omega$ cm)	$\rho(T=296\text{ °K})$[b] / ρ_0
(Pure Pd)	10.57	0.027 31	0.026 73	395
0.32	10.65	0.1131	0.1120	95
0.55	11.10	0.1953	0.1928	58
1.0	11.46	0.3211	0.3167	36

[a] The recomputed ρ_0 is found by subtracting $A(4.2)^2$ from the value for resistivity ρ ($T = 4.2$ °K). A is from the zero-pressure run in eacn case (see Table II).

[b] This resistivity ratio incorporates the "Recomputed ρ_0."

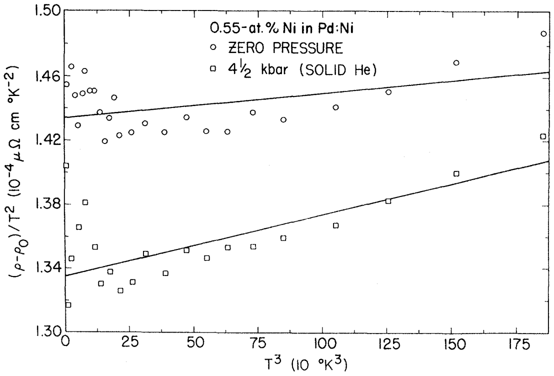

FIG. 9. $[\rho(T) - \rho_0]/T^2$ vs T^3 for the Pd : Ni alloy containing 0.55-at.% Ni.

IV. DISCUSSION OF RESULTS

A. Effect of Pressure on T^2 Contribution–Comparison with Theory

Application of pressure (~ 4.5 kbar) results in a decrease in the T^2 contribution to the electrical resistivity $[A(c)T^2]$ for pure Pd and for each of the alloys measured. For pure Pd the decrease in $A(0)$ is just within the limits of the experimental resolution (Table II). For a pressure of 4.5 kbar this effect increases with the concentration of Ni for alloys containing 0.32- and 0.55-at.% Ni, but the size of the decrease in $A(c)$ for the alloy containing 1-at.% Ni is intermediate between the values for the above two alloys.

The results of the measurements made at an intermediate pressure (2.3 kbar) for the alloy containing 1-at.% Ni indicate that the decrease in $A(c)$ is linear with respect to volume change.

The effect of pressure on the T^2 contribution to the electrical resistivity of the alloys shows qualitative and quantitative disagreement with the estimate given in Sec. IB [see Eq. (10)]. The qualitative disagreement is illustrated in Fig. 11 in which $(\Delta A/A)$ for a pressure of 4.5 kbar is plotted versus $[A(c) - A(0)]/A(c)$. The linear variation predicted by Eq. (10) is clearly not satisfied. Quantitatively, the magnitude of the decrease of $A(c)$ with application of pressure is found to be larger by about a factor of 3 or 4 than that predicted by Eq. (10).

The quantiative disagreement is not surprising. Aside from the approximation that s to d transfer (associated with a small change in volume) can be neglected, the prior calculations contain another possibly unjustifiable approximation. The expression for $A(c)$ [Eq. (7)] derives from transport theory coupled with the LEEM in the single-impurity limit. The magnetostriction results[14] were fitted to the LEEM in the many-impurity limit which predicts a quite different form for the concentration dependence of $\partial \ln\chi(c)/\partial \ln V$. From Eqs. (2) and (4) it follows that

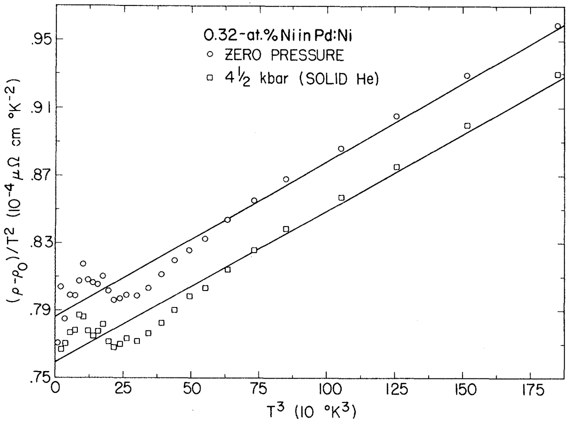

FIG. 8. $[\rho(T) - \rho_0]/T^2$ vs T^3 for the Pd : Ni alloy containing 0.32-at.% Ni.

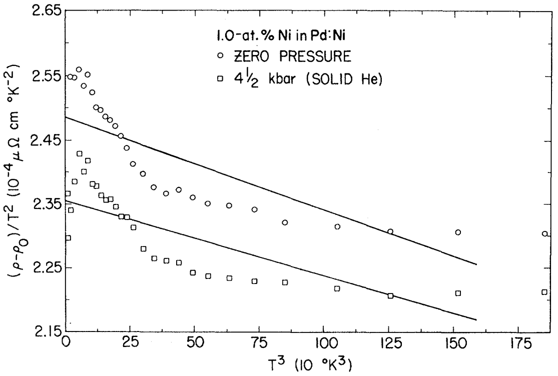

FIG. 10. $[\rho(T) - \rho_0]/T^2$ vs T^3 for the Pd : Ni alloy containing 1.0-at.% Ni.

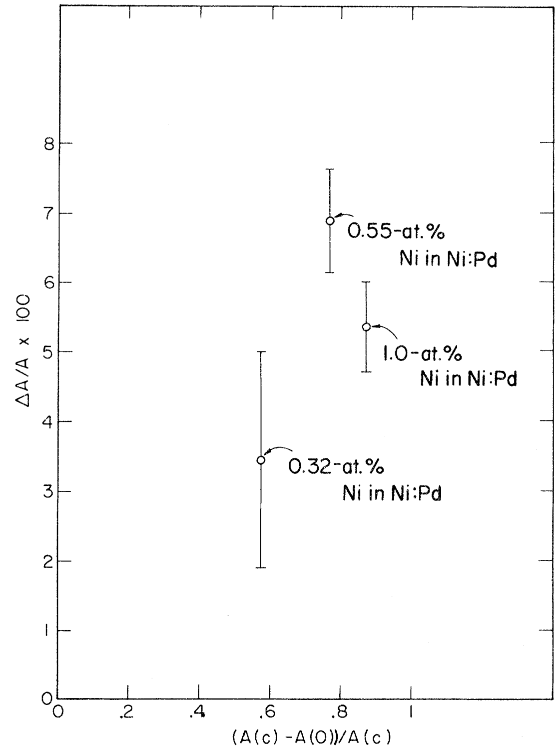

FIG. 11. Relative change in the coefficient of the T^2 contribution to the electrical resistivity with pressure ($\Delta A/A$) vs $[A(c)-A(0)]/A(c)$ for a pressure of 4.5 kbar. $[A(c)-A(0)]/A(c)$ in the abscissa is evaluated at this pressure.

$$\frac{\partial \ln\chi(c)}{\partial \ln V} \propto \frac{\chi(c)-\chi(0)}{\chi(c)}$$

in the single-impurity limit and

$$\frac{\partial \ln\chi(c)}{\partial \ln V} \propto \frac{\chi(c)-\chi(0)}{\chi(0)}$$

in the many-impurity limit. The size of the magnetostriction effect is directly proportional to $\partial \ln\chi(c)/\partial \ln V$. Since the magnetostriction results fit the prediction of the LEEM in the many-impurity limit that the size of the effect is proportional to the *absolute* change in the susceptibility, it follows that the analogous prediction of the LEEM in the single-impurity limit with respect to the *relative* change in the susceptibility is incorrect.

This suggests that the relaxation-time calculation, from which Eq. (7) is derived, should be redone using the paramagnon energy spectrum from the many-impurity limit of the LEEM in order to obtain an expression for $A(c)$ valid in the many-impurity limit. The new calculation of the volume dependence of $A(c)$ could then proceed as above.

The qualitative disagreement concerning the failure of $\Delta A/A$ to exhibit a monotonic single-valued increase with respect to $[A(c)-A(0)]/A(c)$ (Fig. 11) is more serious and is not expected to be remedied simply by this improvement in the calculation of $A(c)$. This result suggests that the range of concentration of Ni for which the LEEM is valid may be somewhat less than 0- to 1-at.% Ni, as has previously been suggested.[2,7] However, as noted in Sec. IV B, the value obtained for $\Delta A/A$ is sensitive to the choice of exponent for the contribution of order higher than T^2 for the 1-at.% alloy. Thus, the qualitative discrepancy noted above may be the result of inadequacies in the model for electron-paramagnon scattering.

It should be noted that there is not direct disagreement between the present studies and the magnetostriction studies of Fawcett *et al.*[14] Our results are consistent with their conclusion that, in the framework of the LEEM (many-impurity limit), the strain dependence of the effective impurity potential of the alloys is large and positive. This leads to the prediction that the volume derivative of $A(c)$ is large and positive or, alternatively, that the pressure derivative of $A(c)$ is large and negative [Eq. (10)]. Our data are in qualitative agreement with this prediction for each of the alloys investigated.

B. Effect of Pressure on Contribution of Terms of Order Higher than T^2

The pressure dependence of the coefficient of the T^5 contribution (B) exhibits a complex behavior with respect to the concentration of Ni for the alloy data (Table II). The pure-Pd sample and the sample containing 0.32-at.% Ni show only a small decrease in a comparatively large value of B with the application of 4.5 kbar of pressure. For the alloy containing 0.55-at.% Ni, the value of B is quite small, and the application of 4.5 kbar of pressure produces a large increase in the zero-pressure value. For the alloy containing 1-at.% Ni, the value of B is large and negative, and the application of 4.5 kbar of pressure results in a rather large decrease in the size of B.

The above phenomena are consistent with the idea that electron-paramagnon scattering gives rise to a contribution to the low-temperature electrical resistivity of order higher than T^2 with a negative coefficient. As pointed out in Sec. I B, one might expect the size of such a contribution to decrease with increase in pressure since, as this experiment has demonstrated, the size of the T^2 contribution decreases with increase in pressure.

Assuming that the T^5 contribution for pure Pd arises from electron-phonon scattering, and comparing the value of B for the alloy containing 0.32-at.% Ni with the value of B for pure Pd, it is seen that the negative contribution from electron-paramagnon scattering is not very large for this alloy.

The small decrease in B with pressure exhibited by these two samples presumably reflects the change in electron-phonon scattering (ρ_{ph}) due to pressure. Assuming the Bloch–Grüneisen form for ρ_{ph} at low temperatures,

$$\rho_{ph} = \frac{C}{\theta_R}\left(\frac{T}{\theta_R}\right)^5 , \tag{13}$$

where C is not expected to depend significantly on volume. θ_R is a characteristic temperature deduced from $\rho(T)$ and characterizes the degree of excitation of the vibrational modes of the lattice at any temperature. Its volume dependence (if not its numerical value) should be the same as the volume dependence of the Debye temperature (which experimentally is deduced from the low-temperature specific heat) and is given by the Grüneisen constant

$$\gamma_G = -\frac{d\ln\theta_R}{d\ln V} .$$

Then, from Eq. (13)

$$\frac{d\ln\rho_{ph}}{d\ln V} = 6\gamma_G$$

or

$$\frac{\Delta\rho_{ph}}{\rho_{ph}} \simeq \frac{\Delta V}{V}\,(6\gamma_G) .$$

Taking $(\Delta V/V)\times 100 = -0.24$ corresponding to a pressure of 4.5 kbar and $\gamma_G \approx 2.3$ for Pd we have

$$(\Delta\rho_{ph}/\rho_{ph})\times 100 \approx -3.3. \tag{14}$$

For 4.5 kbar of pressure, the relative change in B for the pure-Pd sample and for the alloy containing 0.32-at.% Ni (Table II) is somewhat less than the value of 3% predicted by Eq. (14). Considering the experimental uncertainty in these values for B this is not surprising. A better indication of the reduction in the electron-phonon scattering with pressure is seen from inspection of the higher-temperature resistivity data for pure Pd (Fig. 3). It is evident that in the upper part of the temperature range (9–11.49 °K) the pressure measurements fall significantly below the zero-pressure measurements for each temperature and the spacing is increasing with temperature.

For the sample containing 0.55-at.% Ni, the negative contribution from electron-paramagnon scattering, although nearly equal in size to the contribution from electron-phonon scattering, changes more rapidly with increase in pressure. The decrease in size of the negative contribution from electron-paramagnon scattering gives rise to a net *increase* in B (Table II) with 4.5 kbar of pressure.

For the alloy containing 1-at.% Ni the negative (and higher order than T^2) contribution from electron-paramagnon scattering has completely swamped out the contribution from electron-phonon scattering, and the effect of pressure is a net (large) decrease in the size of B.

It is evident from Figs. 6 and 10 that Eq. (11) is not an adequate description for the temperature-dependent resistivity of the alloy containing 1-at.% Ni. It is also evident that the magnitude of the value for B extracted from such a fit is quite sensitive to the maximum temperature used in the fit. Table IV shows the result of using a lower-temperature cutoff for the best least-squares fit to Eq. (12) and the result of replacing the T^5 term in Eq. (11) by a T^4 term and a T^3 term, respectively. The uncertainty in the values of ρ_0 and A is rather insensitive to the presence of a contribution of order higher than T^2, and the experimental uncertainties given in Table II remain valid for the values of ρ_0 and A deduced from the above fits. The fit steadily improves as the exponent of the contribution of order higher than T^2 is lowered from 5 to 4 to 3. The relative change in B_n (for $n = 3$, 4, or 5) associated with the application of 4.5 kbar of pressure varies only slightly among the above fits.

On the other hand, the relative change in A (for the alloy containing 1-at.% Ni) for a pressure of 4.5 kbar and for $n = 3$ has significantly increased over the value for $n = 5$ (~ – 5.3%) and is about the same size (~ – 7%) as $\Delta A/A$ for the alloy containing 0.55-at.% Ni. Insofar as this fit is meaningful, our results for $\Delta A/A$ as a function of concentration of Ni are no longer inconsistent with the LEEM (single-impurity limit). Decreasing the value of n from 5 is not expected to result in a significantly different value for $\Delta A/A$ for the alloys with lower concentrations of Ni, since the deviation from the fit for $n = 5$ is not nearly so large, presumably because the contribution from electron-paramagnon scattering of order higher than T^2 is much smaller for the lower-concentration alloys.

Figure 12 shows that even for the fit with $n = 3$, the data for the alloy containing 1-at.% Ni exhibit a systematic deviation which indicates that an exponent lower than 3 would give an even better fit. One is thus led to doubt the validity of using Eq. (11) to describe the temperature dependence of the alloys below 10 °K. Our results indicate that in this temperature range there is negative deviation from T^2 behavior of order higher than T^2 but less than T^5. Upon application of pressure this contribution is reduced in size more rapidly than is the T^2 contribution itself.

For pure Pd and for the alloys containing 0.32- and 0.55-at.% Ni the plots of $(\rho - \rho_0)/T^2$ vs T^3 (Figs. 7–9) for both the zero-pressure data and the pressure data show a peculiar systematic deviation from the best fit to Eq. (12) at the lower temperatures. T was known only to ± 20 m°K and that probably accounts for these systematic deviations

TABLE IV. Summary of results of least-squares fit of data for alloy containing 1 at.% to $(\rho-\rho_0)/T^2 = A + B_n T^{n-2}$ for $n = 3, 4, 5$.

n	Relative volume change $\frac{\Delta V}{V}\times 100$	ρ_0 ($\mu\Omega$ cm)	$A\times 10^6$ ($\mu\Omega$ cm/°K^2)	$B_n\times 10^9$ ($\mu\Omega$ cm/°K^n)	$\frac{\delta B_n}{B_n}\times 100$[a]	$(CHI)^2\times 10^9$ ($\mu\Omega$ cm/°K^2)^2	Maximum temperature used in fit (°K)
3	0	0.33569	283	−5520	5.0	0.185	10.17
	−0.239	0.33224	263	−4370	4.9	0.112	10.17
4	0	0.33576	261	−348	8.2	0.314	10.17
	−0.239	0.33229	246	−281	7.6	0.176	10.17
5	0	0.33579	254	−28.2	12	0.452	10.17
	−0.239	0.33232	240	−23.0	11	0.257	10.17
5	0	0.33583	249	−14.4	15	0.784	12.28
	−0.239	0.33235	236	−11.7	15	0.493	12.28

[a] Relative uncertainty in value of B due to scatter of measured resistivities from best fit to equation given in caption.

around 6 °K where we changed control schemes. This has little effect on our qualitative conclusions.

It is evident that very precise thermometry as well as precise resistivity measurements are required to determine the nature of the deviation from T^2 behavior in the low temperature resistivity ($T < 10$ °K) for the alloys.

C. Effect of Pressure on Residual Resistivity

The residual resistivity of each of the alloys undergoes a reversible decrease of about 1% upon application of 4.5 kbar of hydrostatic pressure. The residual resistivity of pure Pd also shows a decrease well beyond the limits of the experimental resolution upon application of this pressure (see Sec. III B and Table II). Data for an intermediate-pressure run on the alloy containing 1-at.% Ni (Table II) indicate that the (reversible) decrease in residual resistivity is linear with respect to volume change. For the alloys the 1% decrease noted above is quite large since this is a factor of 4 greater than the change in volume. A significant transfer of low-mobility d electrons to high-mobility s states might account for this remarkable behavior.

In the absence of a conduction band at zero temperature the Fermi level would maintain its relative position within the d band as the width of the band increases with application of pressure. In the presence of a conduction band, this simple picture breaks down, since compression of the crystal causes carriers to be transferred between the d band and the conduction bands. Two distinct effects produce this transfer. As the lattice constant decreases, the spacing between conduction levels increases, and, if the bottom of the conduction band were to remain fixed relative to the top of the d band, conduction states would move up through this region emptying electrons into the d band as they passed through the Fermi level. This effect, by itself, would produce an increase in resistivity by removing some of the more mobile carriers. However, compression also leads to a downward movement of the bottom of the conduction band, which, in itself, implies a transfer of carriers in the opposite direction. There are indications that this effect may be characteristic of the entire transition series.[31] It occurs because, under compression, the mean d-band energy stays roughly constant relative to the atomic zero, while the zero of the "muffin-tin" ionic potential, which gives the approximate position of the bottom of the conduction band, moves downward with respect to this point as the distance between ionic potentials decreases. Lang and Ehrenreich[31] show that for Ni and Ni-Cu alloys the second of the two opposing mechanisms for charge transfer is more important. If this is also true for Pd and very dilute Pd : Ni

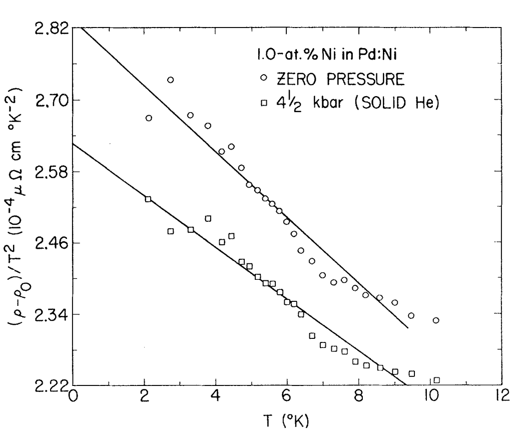

FIG. 12. $[\rho(T)-\rho_0]/T^2$ vs T for the Pd : Ni alloy containing 1.0-at.% Ni. The solid lines show the result of the best fit of the data to $(\rho-\rho_0)/T^2 = A + B_3 T$.

alloys, the resulting relative increase of high-mobility s-like electrons at the expense of the population of low-mobility d-like states would result in a decrease in the residual resistivity with pressure as is seen in this experiment.

For small concentrations of Ni (< 1 at.%) both the total residual resistivity of the alloys and the (absolute) decrease in the residual resistivity with pressure are proportional to the concentration of Ni. This suggests a simple model for the role of the Ni in the pressure effect.

There are two ways in which the addition of Ni in Pd can bring about an increase in the residual resistivity. Each Ni ion is expected to behave as a defect, giving rise to local strains in the surrounding lattice. Since Ni and Pd are isoelectronic, the resulting increase in residual resistivity is small, as previously noted. It might also be true that the addition of Ni tends to fill the d band which is known to contain about 0.36 holes/atom in Pd.[9] This could only occur at the expense of the population of carriers in the conduction band, which will also result in an increase in the residual resistivity. Then for a series of alloys with successively larger concentrations of Ni, a characteristic increase in the population of carriers in the conduction band for a given pressure should result in a larger *absolute* decrease in the residual resistivity for each case, since a fixed amount of s to d transfer represents a larger *relative* increase in the population of carriers in the conduction band for each alloy.

The above model indicates that the Ni plays a passive role and that the large decrease (with pressure) in the residual resistivity of the alloys is a manifestation of the intrinsic properties of Pd. Similar investigation of other alloys, e.g., Pd : Ag, would help to clarify the nature of this effect.

V. CONCLUSION

Measurements of the low-temperature electrical resistivity of pure Pd and a series of very dilute Pd : Ni alloys (0.32-, 0.55-, and 1.0-at.% Ni) have been carried out under hydrostatic pressure (~4.5 kbar) using solid helium as the pressure medium.

It has been found that the coefficient of the T^2 contribution believed to arise from paramagnon-enhanced electron-electron scattering is reduced upon application of pressure for each alloy by an amount greater than that estimated on the basis of a localized-exchange-enhancement model coupled with earlier magnetostriction work.[14] Ambiguities in curve fitting, particularly for the alloy containing 1-at.% Ni, make it difficult to conclude whether the concentration dependence of this effect agrees qualitatively with existing localized-enhancement models.

The results are consistent with the idea that electron-paramagnon scattering gives rise to a negative deviation from T^2 behavior—of order greater than T^2 and less than T^5—in the alloys which is more strongly reduced in size upon application of pressure than is the T^2 contribution itself. For the alloy containing 1-at.% Ni both the zero-pressure data and the pressure data indicate that a description of the temperature-dependent resistivity $\rho(T)$ for $T < 10\,^\circ\mathrm{K}$ by $\rho = \rho_0 + AT^2 + BT^5$, as has previously been suggested, is inadequate.

A large reversible decrease in the residual resistivity of each of the alloys was observed upon application of pressure. The relative size of this effect is four times as large as the relative volume change. This suggests that there may be a significant transfer of low-mobility d electrons to high-mobility s states with application of pressure. A simple model is offered to explain the role of the Ni in this effect.

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[†] Based on a Ph. D. dissertation submitted to the University of Illinois by R. A. Beyerlein.

[‡] Present address: Solid State Science Division, Argonne National Laboratory, Argonne, Ill. 60439.

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

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

[3] S. Englesberg, W. F. Brinkman, and S. Doniach, Phys. Rev. Letters 19, 1040 (1968).

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

[5] G. Chouteau, R. Fourneaux, K. Gobrecht, and R. Tournier, Phys. Rev. Letters 20, 193 (1968); G. Chouteau, R. Fourneaux, R. Tournier, and P. Lederer, *ibid.* 21, 1082 (1968).

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

[7] J. T. Schriempf, A. I. Schindler, and D. L. Mills, Phys. Rev. 187, 959 (1969).

[8] A. B. Kaiser and S. Doniach, Intern. J. Magnetism 1, 11 (1970).

[9] J. J. Vuillemin and M. G. Priestly, Phys. Rev. Letters 14, 307 (1965); J. J. Vuillemin, Phys. Rev. 144,

396 (1966).

[10] L. R. Windmiller, J. B. Ketterson, and S. Hornfeldt, Phys. Rev. B 3, 4213 (1971).

[11] F. M. Mueller, A. J. Freeman, J. O. Dimmock, and A. M. Furdyna, Phys. Rev. B 1, 4617 (1970).

[12] F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) A240, 42 (1957).

[13] See, J. R. Schrieffer, J. Appl. Phys. 39, 642 (1968).

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

[15] Some work has been done on the effect of hydrostatic pressure on the magnetic moment of *ferromagnetic* Pd : Ni alloys. See, H. Fujiwara, N. Tsukiji, N. Yamate, and E. Tatsumoto, J. Phys. Soc. Japan 23, 1176 (1967).

[16] For the original calculation of the dynamical susceptibility $\chi(k,\omega)$ applicable to pure Pd see, T. Izuyama, D. J. Kim, and R. Kubo, J. Phys. Soc. Japan 18, 1025 (1963).

[17] J. Mathon, Proc. Roy. Soc. (London) A306, 355 (1968).

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

[19] This is an approximate value for the compressibility of Pd at room temperature. The compressibility at 0 °K should not be much changed since the bulk modulus $[V^{-1} \times (\partial V/\partial p)]^{-1}$ depends on the total free energy, and the contribution of excited states to the total free energy is small.

[20] H. F. Sterling and R. W. Warren, Metallurgia 67, 301 (1963).

[21] R. A. Beyerlein, thesis (University of Illinois, Urbana-Champaign, 1972) (unpublished).

[22] The four- (Cu) conductor swaged tubing was supplied by Continental Sensing, Inc. This firm has since gone out of business. A similar product may be obtained from American-Standard, Aeroresearch Dept., 9000 King St., Franklin Park, Ill. 60131.

[23] Epoxi-Patch Kit No. 6c, Aluminum Grey—supplied by the Dexter Corp., Hysol Division, Olean, N. Y. 14760.

[24] There was always more noise ($\sim\pm 4$–6 nV) present in the low-temperature measurements.

[25] Room-temperature tests showed the bursting pressure of this tubing (Superior Tube Co., 1938 Germantown Ave., Norristown, Pa. 19404) to be 105 000 psi.

[26] W. D. Seward, D. Lazarus, and S. C. Fain, Jr., Phys. Rev. 178, 345 (1969).

[27] Heise Bourdon Tube Co., Inc., Newtown, Conn. 06470.

[28] J. S. Dugdale, Nuovo Cimento Suppl. 9, 27 (1958).

[29] J. T. Schriempf, Phys. Rev. Letters 20, 1034 (1968).

[30] P. W. Bridgman, *Physics of High Pressures* (G Bell, London, 1949), p. 160.

[31] N. D. Lang and H. Ehrenreich, Phys. Rev. 168, 605 (1968).

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Effect of Crystal Fields on the Magnetic Properties of Samarium Intermetallic Compounds

H. W. de Wijn
Fysisch Laboratorium der Rijksuniversiteit van Utrecht, Utrecht, The Netherlands

and

A. M. van Diepen and K. H. J. Buschow
Philips Research Laboratories, Eindhoven, The Netherlands

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Neither of the intermetallics $SmAl_2$ (a ferromagnet below $T_C = 120$ K) and $SmSn_3$ (an antiferromagnet below $T_N = 11$ K) show the sign reversal predicted by White and Van Vleck for the $4f$-induced Knight shift in the paramagnetic region. On the other hand, no particular anomaly has been observed in the temperature dependence of the susceptibility. An explanation for this is given in terms of mixing of excited J levels of Sm^{3+} into the $J = \frac{5}{2}$ ground multiplet by cubic crystal fields. The calculation is described of the crystal field matrix elements of Sm^{3+} between any J and J', and expressions are derived for the Knight shift and the susceptibility in the presence of crystalline and molecular fields. It is shown that the sixth-order component of the crystal field is important, and that the anomalous behavior is enhanced by ferromagnetic exchange between the Sm ions. A study of the lattice constants and the ^{27}Al quadrupolar coupling in comparison with other RAl_2 (R = rare earth) compounds excludes the possibility of Sm in $SmAl_2$ not being trivalent.

I. INTRODUCTION

In rare-earth intermetallic compounds the orbital as well as the spin part of the localized $4f$ magnetism is accessible to experimental study. In the paramagnetic region, the $4f$ magnetic susceptibility χ_f is a direct measure for the rare-earth magnetic moment, i.e., $\langle L_z + 2S_z \rangle$, while the part of the Knight shift at a nonmagnetic site due to s-f exchange enhancement of the conduction-electron-spin polarization K_f is proportional to $\langle S_z \rangle$. Within the ground multiplet of the rare earth, $\langle L_z + 2S_z \rangle$ and $\langle S_z \rangle$ are proportional to each other, differing by a factor $(g_f - 1)/g_f$, with g_f the Landé g factor.