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# *Pd* V: A System with a High Spin-Fluctuation or Kondo Temperature?*

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The temperature dependence of the incremental resistivity $\Delta\rho(T)$ of five dilute *Pd* V alloys, ranging in concentration from 0.15- to 1.0-at.% V, has been measured from 1.4 to 300 K. $\Delta\rho\ (T=0)$ increases linearly with V content at a rate of $3.26 \pm 0.13\ \mu\Omega$ cm/at.% V. Between 10 and 80 K, $\Delta\rho(T)$ increases rapidly with increasing temperature, in a manner characteristic of Matthiessen's-rule breakdown resulting from phonon and impurity scattering with differing anisotropies. Above 80 K, however, $\Delta\rho(T)$ *decreases* smoothly with increasing temperature; various attempts have been made to fit this *high-temperature* variation: (i) In terms of a localized-spin-fluctuation (lsf) model, these data are well fitted by $\Delta\rho(T) = C + D\ \ln[(T^2+\theta^2)^{1/2}]$, with lsf temperature $\theta$ estimated at about 160 K for isolated impurities. $D$, however, does not scale linearly with the V concentration $c$, and it is necessary to postulate that interimpurity interactions significantly raise $\theta$ for the interaction pair, then $D \propto c(1-c)^n$. The observed variation of $D$ can be approximately reproduced for $n = 150$. (ii) These high-temperature data are also equally well fitted by the Appelbaum–Kondo expression: $\Delta\rho(T) = E\{1-(16\cos 2\delta_v/3\cos^2\delta_v)[(T/T_K)\ln(T/T_K)]^2\}$. The scaling parameter $E$ increases linearly with $c$ and the Kondo temperature $T_K$ is estimated at about 2300 K. Possible variations in the potential phase shift $\delta_v$ indicate that the amount of $s$-band screening *may* increase as $c$ increases. Further experiments are necessary, however, to determine the eventual applicability of either model. Finally, estimates are made of the Matthiessen's-rule deviations $\Delta(T)$, which are then fitted within the framework of a "parallel conduction" model, in which $1/\Delta(T) = 1/\alpha\rho_h(T) + 1/\beta\rho_i(T)$. $\rho_h(T)$ is the host and $\rho_i(T)$ the impurity resistivity. A concentration independent value for $\alpha$ of $0.31 \pm 0.04$ is obtained, but $\beta$ is found to vary with concentration around a value of 0.06.

## I. INTRODUCTION

While alloys of Pd containing first-row transition metals from Cr to Ni have occupied the attention of both experimentalists and theoreticians for many years, relatively little effort has been expended on *Pd*V—the "suspicion" being that it is nonmagnetic. Paradoxically studies of V in Au have revealed a wealth of information on the properties of a Kondo system[1] well below its Kondo temperature,[2–5] and of the effects of interimpurity interactions in such a system.[6] Of the work that has been done on *Pd*V, thermopower ($S$) measurements[7] up to 800 K reveal that V produces a positive contribution to $S$ over almost all of this temperature range, this contribution being the largest relative to that produced by all other first-row transition-metal impurities at 800 K. The possibility of a high-temperature Kondo bound state was briefly discussed.[7] The measured susceptibility[8] of a Pd-2-at.%-V alloy is lower than that of "pure" Pd at all temperatures below 300 K, while the incremental resistivity $\Delta\rho(T)$ of the same sample appears to be temperature independent below 20 K, increasing with temperature in the range 20–60 K; no measurements of $\Delta\rho(T)$ above 60 K were reported. Theoretical studies[9,10] based on both the Anderson[11] and the tight-binding models[12,13] indicate that *if* V does carry a magnetic moment in Pd, the induced $d$-band polarization will be negative, as for Cr.

Recently there had been considerable progress made towards a unified description of the behavior of such transition-metal impurities in Pd (and other hosts). Based on a phase-shift calculation[14-16] which phenomenologically introduced potential scattering of arbitrary strength into the Kaiser–Doniach[17] (KD) localized-spin-fluctuation (lsf) model, this phase-shift approach modified the KD universal curve for the incremental resistivity $\Delta\rho(T)$ into[16]

$$\Delta\rho(T)/c = A + B\ln[(T^2+\Theta^2)^{1/2}], \tag{1}$$

where $\Theta$ is identified with the lsf characteristic temperature $T_s$[17] and $A$ and $B$ are constants. This phenomenological treatment has recently been placed on firmer foundations by the more formal approach of Rivier and Zlatic[16]; the temperature dependence of the incremental resistivity calculated by these latter authors on the basis of scattering from lsf substantially "verifies" that inferred from Eq. (1). [Working from the opposite limit—the strongly magnetic-impurity limit—several authors[18] suggest that Eq. (1) should result when intermediate impurity (scattering) states are subject to relaxation effects.]

The principal achievement of the phase-shift model has been to predict the correct sign for $B$ in alloys of the first-row transition-metal impurities in Pd (and other hosts)—see Table I. The predicted sign of $B$ for V is negative. Further, we note the variation of spin-fluctuation temperature $T_s(\Theta)$ with such impurities in Pd is reminiscent of the

TABLE I. Sign of $B$ from the phase-shift model for Pd alloys.

| Impurity | $T_s(\Theta)$ (K) | Sign of $B$ (phase-shift model) | Sign of $B$ (observed) |
|---|---|---|---|
| Ni | $\sim 80$ | + | + |
| Co | $<1$ | + | + |
| Fe | $\ll 1$ | + | + (Pt, Ref. 16) |
| Mn | $\ll 1$ | − | ? |
| Cr | $\sim 30$ | − | − |
| V[a] | $\sim 160$ | − | − |

[a]See Sec. III in text.

variation of the Kondo temperature $T_K$ with the same impurities in noble metals,[19] being low at the center of the series (Mn) and increasing towards its ends (V and Ni).

In this paper we report on electrical-resistivity measurements on several dilute *Pd*V alloys (containing up to 1-at.% V) over the temperature range 1.4–300 K. The observed incremental resistivities $\Delta\rho(T)$ are well fitted by Eq. (1), with $B$ negative (as predicted) and with a spin-fluctuation temperature $\Theta$ of about 160 K (comparable with that of Ni in Pd). Resistivity measurements alone however cannot definitively distinguish between the rival claims of relatively rapid (small $\hbar/kT_s$) $d$-level spin fluctuations localized within the impurity cell, or possible Kondo compensation of a V moment by itinerant electrons of the host, since $\Delta\rho(T)$ is equally well fitted by the Appelbaum-Kondo expression,[20] with $T_K$ estimated at about 2000 K.

## II. EXPERIMENTAL DETAILS

Solid solutions of V in Pd extend up to 50-at.% V,[21] and so alloys containing up to 1-at.% V prepared here should certainly retain the fcc structure of the host. Using 99.999%-pure Pd wire and 99.9%-pure V metal (principal impurities; 200 ppm each of Fe and Si), both obtained from Johnson Matthey and Co. (London), alloys of nominal V concentration 0.15, 0.20, 0.50, 0.75, and 1.0 at.% were prepared by successive dilutions of the most concentrated alloy with pure Pd. This most concentrated alloy was itself prepared by melting Pd and V in the appropriate amounts on the water-cooled copper hearth of an argon-arc furnace, using a tungsten electrode. Homogeneity was ensured by repeatedly inverting and remelting each alloy. Melting losses were negligibly small. Resistivity specimens of approximate dimensions 10×0.2 ×0.015 cm were cut from sheets of alloy cold rolled between Melinex to the desired thickness. After etching, washing, and drying, these specimens were annealed *in vacuo* at 1000 °C for 30 h. A pure-metal sample was prepared by similarly cold rolling Pd wire to a thickness of 0.008 cm; this specimen was subsequently treated in the same manner as the alloys.

The specimens were mounted in a holder accommodating all six samples, and their resistances measured using a four-probe technique.[22] Temperatures in the range 1.4–4.2 K were stabilized and measured to ± 5 mK using the $He^4$ vapor pressure; temperatures above 4.2 K were measured to better than ± 0.5% using a nonlinear gas thermometer. The area to length ratio for each specimen was carefully determined to ± 0.3%[23]; the lattice constants used in these ratio determinations were obtained from a linear interpolation of the measured lattice constant of a Pd–1-at.%-V alloy.[24]

## III. RESULTS AND DISCUSSION

In Fig. 1 the measured resistivities $\rho(T)$ of the five alloys examined are plotted against temperature up to 300 K. At low temperatures $\rho(T)$ is well behaved, exhibiting no anomalous features; at temperatures above about 150 K however, $\rho(T)$ clearly increases appreciably slower than linearly with temperature, indicating a temperature-dependent contribution to $\rho(T)$ from the V impurities. The incremental resistivity $\Delta\rho(T)$ is plotted against temperature in Figs. 2–6, and this allows a more detailed examination of these temperature-dependent contributions. From these latter figures the incremental resistivity at zero temperature $\Delta\rho(T=0)$, can be extracted; this scales linearly with the nominal V concentration—see Fig. 7—from which

$$\Delta\rho(T=0)=3.26\pm0.13\ \mu\Omega\ \mathrm{cm/at.\%\ V}\ . \qquad (2)$$

The strong temperature dependence of $\Delta\rho(T)$ between 10 and 70 K evident in Figs. 2–6 (of roughly the same form as that observed in a 2-at.%-V sample[8]) closely resembles that observed in dilute nonmagnetic alloys,[25] for which it originates in the breakdown of Matthiessen's rule owing to the competing effects of impurity and phonon scattering having differing anisotropies. A similar explanation should be valid for the *Pd*V alloys examined here. Above about 80 K, however, *where such deviations from Matthiessen's rule are expected to reach a temperature-independent plateau*,[26] $\Delta\rho(T)$ for all five *Pd*V alloys measured here begins to decrease with increasing temperature. This decrease continues up to the highest temperature attained in this investigation (300 K). Apart from the systematic variation in all the alloys examined, the size of this decrease between 80 and 300 K ($\simeq 0.25\ \mu\Omega$ cm) is nearly an order of magnitude too large to be accounted for by an error in the mea-

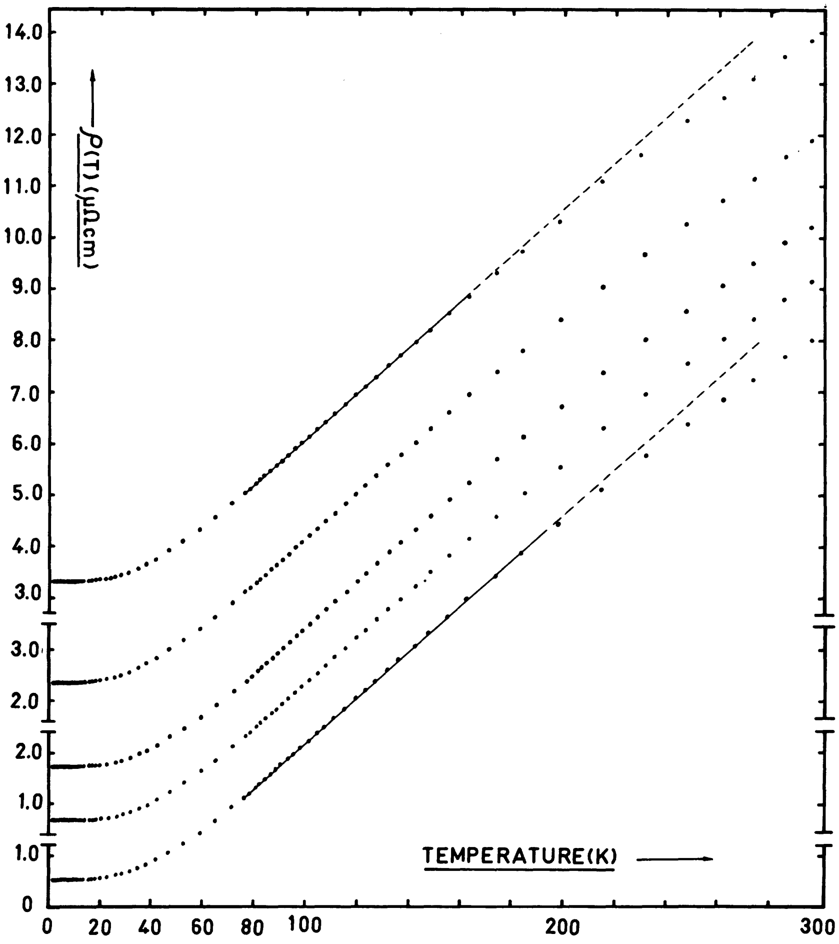

FIG. 1. Measured resistivities $\rho(T)$ (in $\mu\Omega$ cm) plotted against temperature $T$ (in K) up to 300 K for the five alloys examined. The curves are arranged in ascending order of V content.

sured area-to-length ratios. Consequently we next examine possible sources for a temperature dependent $\Delta\rho(T)$.

### A. Spin-Fluctuation Model

Following the discussion in Sec. I, a fit of the experimental data to a temperature dependent $\Delta\rho(T)$ arising from lsf was attempted, using the equation

$$\Delta\rho(T)=C+D\ln[(T^2+\Theta^2)^{1/2}] \tag{3}$$

[this is Eq. (1) rewritten with $C=Ac$ and $D=Bc$ for convenience]. The fitting procedure is based on an evaluation of

$$N^{-1}\left(\sum_{i=1}^{N}[\Delta\rho(T_i)-\Delta\rho(T_i)_{\rm calc}]^2\right)^{1/2}; \tag{4}$$

here $N$ is the number of experimental points (labeled $i$) included in the sum. The best fit was taken as the minimum in Eq. (4), and denoted rmsd (root-mean-square deviation). For the alloys examined here the fit to Eq. (3) was carried out in the temperature region where the contribution to $\Delta\rho(T)$ from Matthiessen's rule breakdown (of the type discussed above) was expected to have reached its temperature-independent (high-temperature) plateau.[26] The curves marked SF in Figs. 2–6 are computed from Eq. (3) using the "best-fit" parameters list in Table II; the full curves in these figures cover the temperature region actually included in the fitting scheme (see Table II), while the dashed portion of these curves are the extension of these computed fits to lower temperatures where again the situation is complicated by the Matthiessen's-rule deviations, previously described. As is evident from these figures the spin-fluctuation model provides an excellent description of the experimental data, the point by point deviation of the computed fit from the measured value being better, on the average, than 3 parts in $10^4$.

At this stage the best-fit parameters deduced from the fitting scheme (and listed in Table II) warrant same comment. Over the composition range investigated $\Theta$ displays a slight (~12%) but not unexpected increase with increasing concentration: Certainly in the Garland approach[18] this is expected, as further interaction effects supply "additional" relaxation channels. Up to about

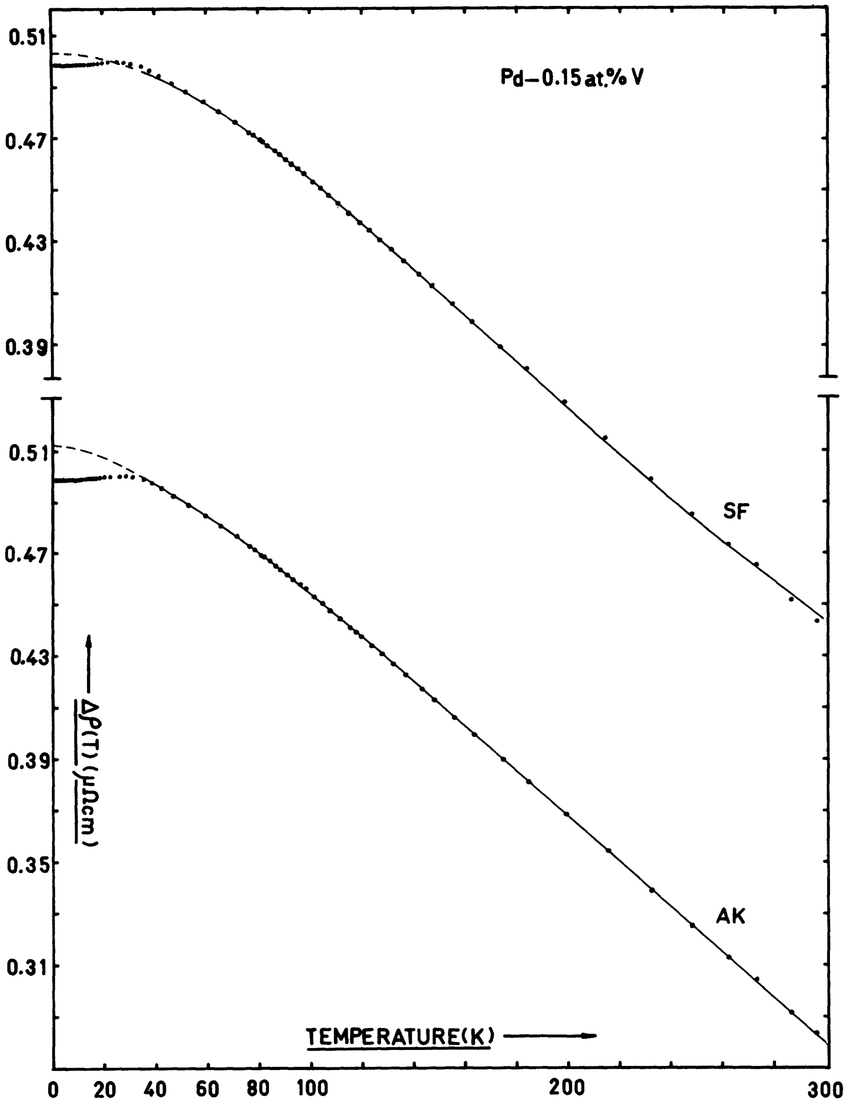

FIG. 2. Incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$cm) plotted against temperature (in K) for the Pd-0.15-at.%-V alloy. The origins of the two curves are explained in the text.

0.5-at.% V however, the spin-fluctuation temperature $\Theta$ is substantially concentration independent, suggesting an "intrinsic" ($c\rightarrow 0$) value of about 155 K for $\Theta$ in this system. As previously pointed out, the measured $\Delta\rho(T=0)$ is linear in the nominal V concentration $c$, as is the "calculated" value of $A'$ $+D\ln\Theta$ [$A'$ is simply the parameter $C$ in Eq. (3) corrected for the Matthiessen's-rule-breakdown "step height"]; however individually neither $A'$ or $D$ scale in a regular manner with impurity concentration. In particular, in an effective-mass treatment of $s$-conduction-electron-impurity spin

TABLE II. Best-fit parameter for $\Delta\rho(T) = C + D\ln[(T^2+\Theta)^{1/2}]$.

| Alloy (at. % V) | $\Theta$ (K) | $C$ ($\mu\Omega$cm) | $-D$ ($\mu\Omega$cm) | rmsd[a] ($10^3$ $\mu\Omega$cm/point) | $A'$ ($\mu\Omega$cm) | Range of fit (K) |
|---|---|---|---|---|---|---|
| 0.15 | 160 ± 3 | 1.96 ± 0.02 | 0.288 ± 0.003 | 0.175 | 1.96 | 41–300 |
| 0.20 | 155 ± 3 | 2.25 ± 0.02 | 0.308 ± 0.003 | 0.184 | 2.23 | 58–300 |
| 0.50 | 169 ± 5 | 3.55 ± 0.05 | 0.345 ± 0.006 | 0.193 | 3.47 | 86–300 |
| 0.75 | 175 ± 7 | 4.76 ± 0.05 | 0.441 ± 0.008 | 0.288 | 4.59 | 86–300 |
| 1.0 | 183 ± 7 | 5.71 ± 0.11 | 0.443 ± 0.015 | 0.272 | 5.59 | 86–300 |

[a] Refers to the temperature range listed in the final column.

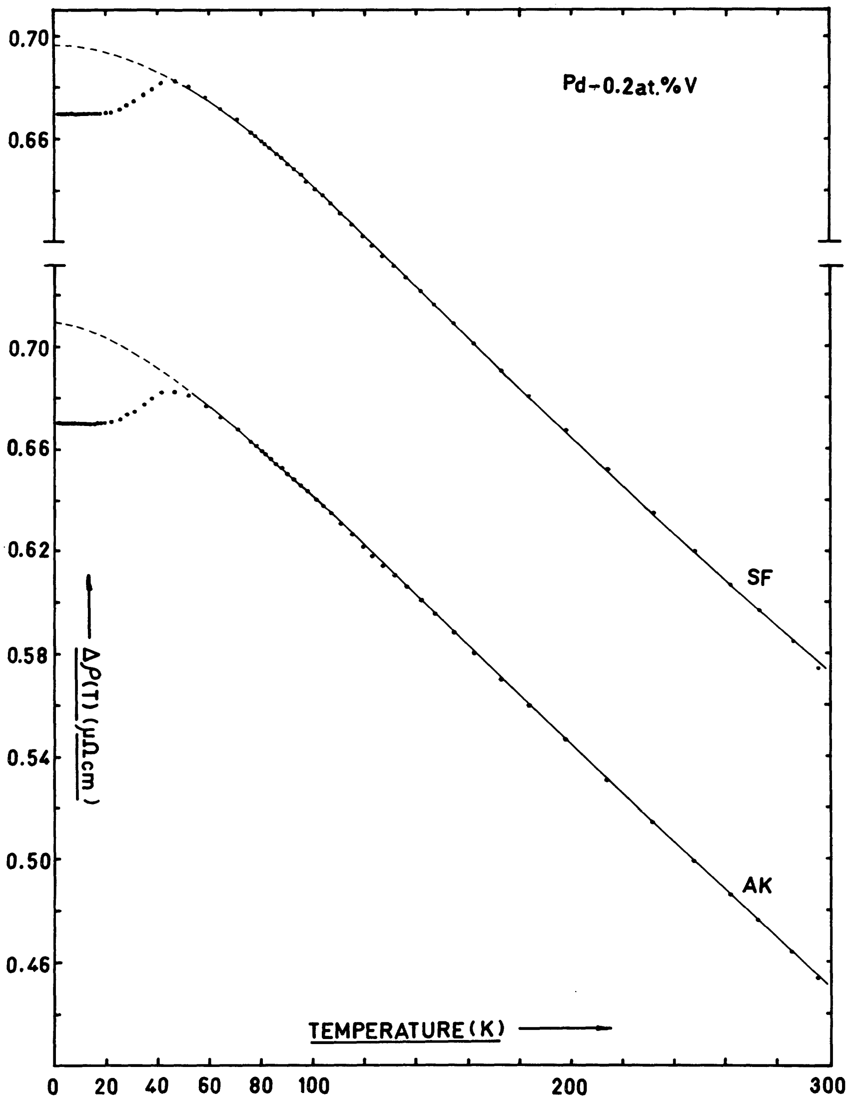

FIG. 3. Incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$cm) plotted against temperature $T$(in K) for the Pd-0.2-at.%-V alloy. See the text for the origin of the two curves.

scattering (in the Garland regime), the coefficient $D$ assumes the form

$$D=\frac{3z}{E_F}\left[\frac{3\pi m^*}{2\hbar e^2 E_F}\left(\frac{\Omega}{N}\right)\right] cJ^3S(S+1) \;, \qquad (5)$$

where $z$ is the number of $s$ conduction electrons per atom with effective mass $m^*$, and $E_F$ is the Fermi energy, $N\Omega^{-1}$ is the number of atoms per unit volume. $J$ is the appropriately weighted wavevector- ($\vec{q}$-) dependent effective exchange coupling (negative in this system). $S$ is the impurity spin. Clearly from Table II, $D$ does not scale linearly with the V concentration, as expected. The apparent paradox of a practically concentration-independent spin-fluctuation temperature $\Theta$ (isolated impurity effect) with the nonlinear variation with concentration of the coefficient $D$, can be resolved to some extent by referring to the situation occurring for V impurities in other hosts. The analysis of susceptibility data[3] on dilute *Au*V alloys, for example, has proceeded on the basis of isolated V atoms being "magnetic," but interaction effects between neighboring V impurities quench this moment (in spin-fluctuation language,[16] impurity interactions raise the spin-fluctuation temperature). Applying this approach to *Pd*V, $\Theta \simeq 155$ K is identified with the spin-fluctuation temperature for isolated V impurities, with the effects of neighboring impurities significantly raising this temperature (for the interacting "pairs"). Certainly, for isolated impurities $\Theta$ is proportional[17] to $[1 - UN(E_F)]$, where $N(E_F)$ is the host density of states at the Fermi energy, and $U$ is the intra-atomic Coulomb repulsion between opposite-spin $d$ electrons at the impurity site (i.e., a measure of the tendency of the state to magnetize). In a qualitative manner this idea can be extended to interacting pairs, using the result[9,10] that neighboring V impurities

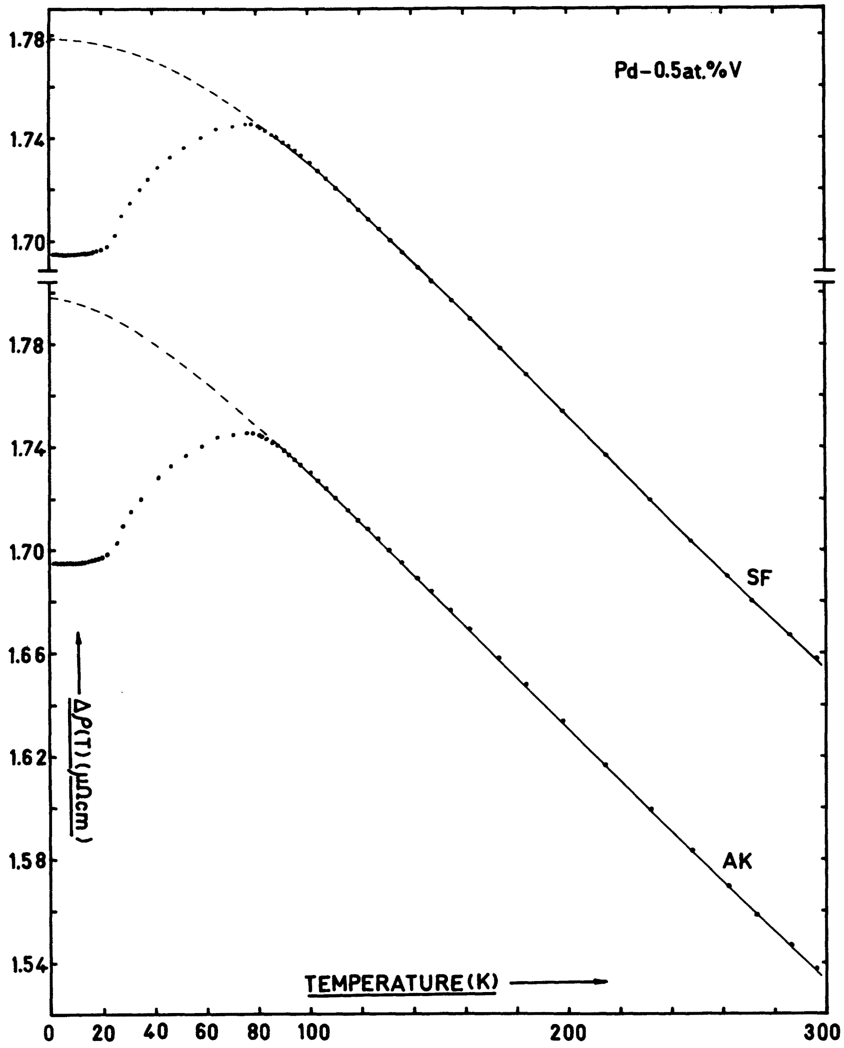

FIG. 4. Incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$cm) plotted against temperature $T$(in K) for the Pd-0.5-at.%-V alloy. The two curves marked SF and AK are explained in the text.

(if they carry a moment) should tend to couple antiparallel, then $U_{\text{eff}}$ for the pair is negative (attraction between opposite spins), resulting in $\Theta$ for the pair being raised.

For a random system, the probability of occupying a central site with the $n$ neighboring sites being unoccupied is simply $c(1-c)^n$. $D$ should then be proportional to this quantity; in this scheme the variation of $D$ with $c$ can be approximately reproduced if $n$ is taken as about 150.[27] In view of the effects of intraband exchange on the spatial extent of the Pd $d$-band response to a spin-dependent potential[28] this value for $n$ does not seem unreasonable.

A final comment in this section regarding the predicted sign and magnitude of the coefficient $D$. Using the ideas of the previous paragraph, the expression for $D$ can be rewritten as

$$D=\frac{3z}{E_F}\left[\frac{3\pi m^*}{2\hbar e^2 E_F}\left(\frac{\Omega}{N}\right)\right] c(1-c)^n J^3 S(S+1)\ . \qquad (6)$$

From the listed values for $D$, the appropriate Pd $s$-band parameters, $S=1$, and the previous estimate for $n$, Eq. (6) yields the values of $J$ listed in Table III. Further, extending the phase shift approach[16] to cover V impurities, then

$$\Delta\rho(T\gg\Theta)-\Delta\rho(0)$$
$$=5c\cos\left(\tfrac{1}{5}\pi Z\right)\sin^2\left(\tfrac{1}{5}\pi S\right)\ \mu\Omega\,\text{cm}\ . \qquad (7)$$

TABLE III. Estimates of the exchange coupling $J$.

| Alloy (at.% V) | $c(1-c)^{150}$ (at.%) | $J$ (eV) |
|---|---|---|
| 0.15 | 0.118 | 0.60 |
| 0.2 | 0.147 | 0.58 |
| 0.5 | 0.234 | 0.52 |
| 0.75 | 0.245 | 0.55 |
| 1.0 | 0.221 | 0.57 |

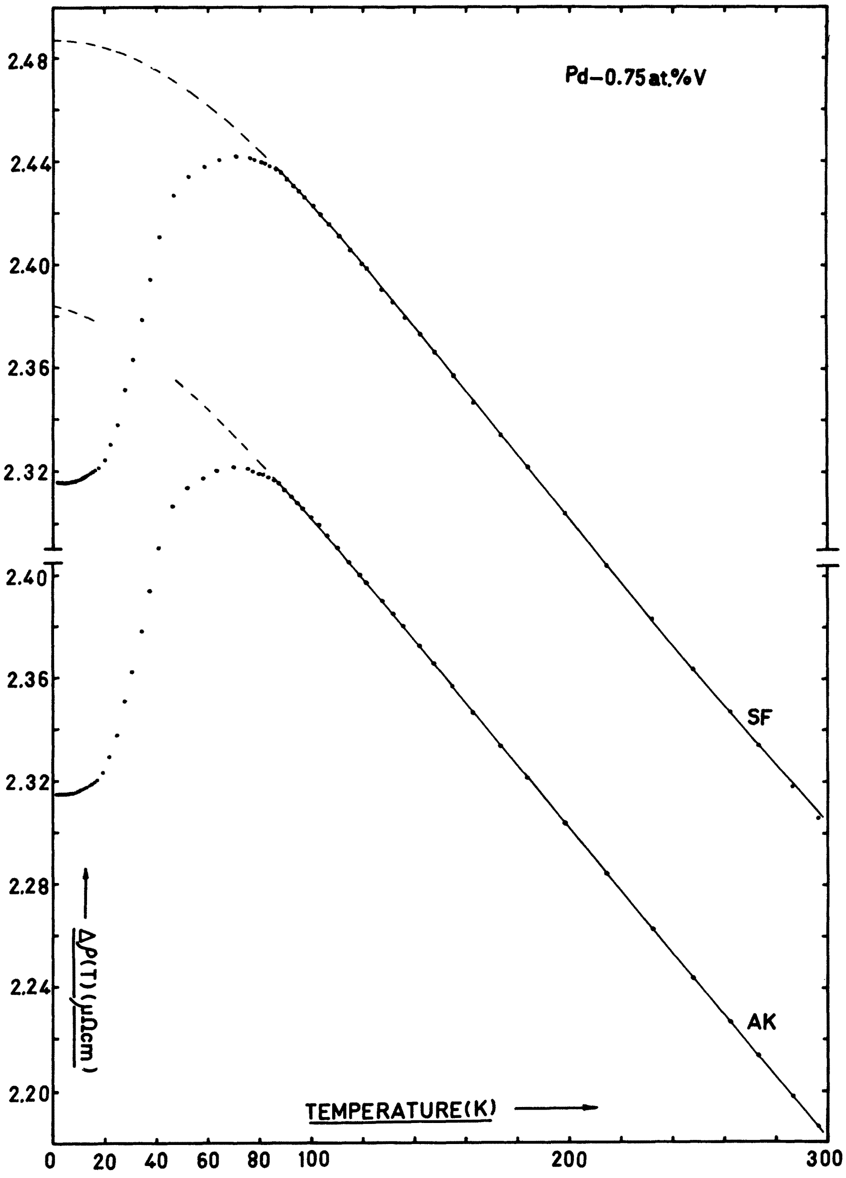

FIG. 5. Incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$cm) for the Pd-0.75-at.%-V alloy plotted against temperature $T$(in K). The two curves are theoretical calculations as explained in the text.

Here $Z$ is the excess impurity nuclear charge. With $Z = -5$ and $S = 1$, then

$$\Delta\rho(0) - \Delta\rho(T \gg \Theta) \simeq 1.8 \ \mu\Omega\,\mathrm{cm/at.\%V}$$

(for $S = 1.5$ a value of $3.25\ \mu\Omega$cm/at.% V is obtained). Clearly this model not only predicts the correct sign for $D$, but also yields a magnitude for the change $\Delta\rho(0) - \Delta\rho(T \gg \Theta)$ which is in reasonably good agreement with that observed experimentally.

### B. Appelbaum-Kondo (AK) Model

In view of the success of the AK expression[20] in reproducing the reasonably low-temperature ($T < T_K$) incremental resistivity for moderate concentrations of first-row transition-metal impurities in noble metals,[23] and in Pd and Pt,[29] then in addition to fitting the high-temperature ($T > 60$ K) data to the spin-fluctuation model the following expression for $\Delta\rho(T)$ was used[20]:

$$\Delta\rho(T) = E\left\{1 - \frac{16\cos 2\delta_v}{3\cos^2\delta_v}\left[\frac{T}{T_K}\ln\left(\frac{T}{T_K}\right)\right]^2\right\} \ . \tag{8}$$

$E$ is a scaling factor, and $\delta_v$, the phase shift introduced by potential scattering. Certainly, serious experimental[29,30] and theoretical[31] doubt has been cast on the validity of Eq. (8); Hamann[31] has indicated that both the functional form and the Kondo temperature $T_K$ of Eq. (8) may be incorrect (certainly Abrikosov's "correct" result[32] for $T_K$ is not reproduced). Experiments[29,30] at very low

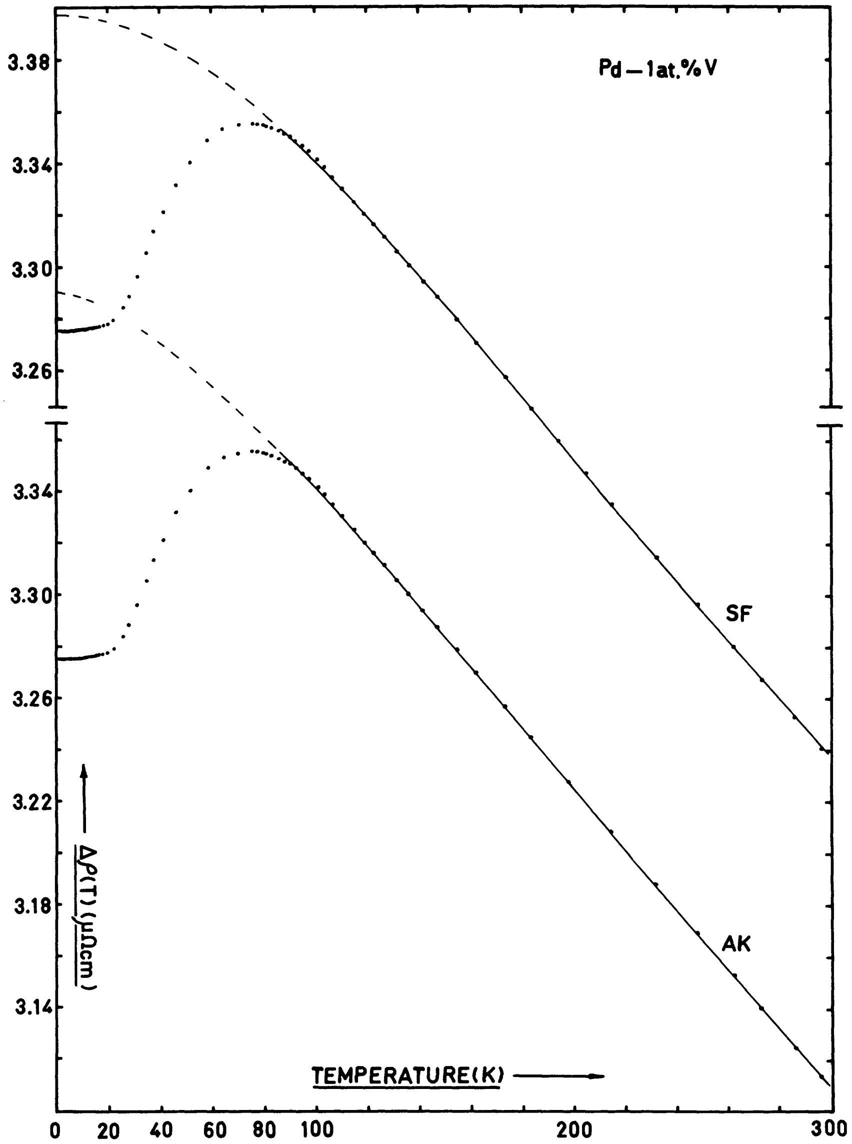

FIG. 6. Incremental resistivity $\Delta\rho(T)$ (in $\mu\Omega$cm) for the Pd-1.0-at.%-V alloy plotted against temperature $T$(in K). The theoretical curves SF and AK are explained in the text.

temperatures ($T \ll T_K$) and concentrations also invalidate Eq. (8); however *Pd*V contrasts with *Pd*Cr in that the temperature variation of $\Delta\rho(T)$ is much stronger in the latter system, thus allowing accurate estimates of the $T^2$ term in low-concentration alloys in the temperature region where a significant contribution to $\Delta\rho(T)$ from Matthiessen's-rule breakdown has not *begun* to occur. This is not the case in *Pd*V, and we have resorted to fitting Eq. (8) at intermediate temperatures (above about 80 K) and concentrations where the AK treatment has enjoyed some experimental success in other systems, so that *Pd*V can at least be compared within this type of framework with these other systems.

The temperature range covered and the fitting scheme used was identical with that for the spin-fluctuation model. The curves marked AK in Figs. 2–6 are these least-squares fits of the data to Eq. (8). The associated parameters are listed in Table IV.

TABLE IV. Best fit parameters for

$$\Delta\rho(T) = E\left\{1 - \frac{16\cos 2\delta_v}{3\cos^2\delta_v}\left[\frac{T}{T_k}\ln\left(\frac{T}{T_K}\right)\right]^2\right\}.$$

| Alloy (at. % V) | $T_K$ (K) | $E$ ($\mu\Omega$cm) | $\delta_v$ (deg) | rmsd[a] ($10^3$ $\mu\Omega$cm/point) | Range of fit (K) |
|---|---|---|---|---|---|
| 0.15 | 2300 ± 50 | 0.511(8 ± 2) | 0 | 0.130 | 41–300 |
| 0.20 | 2300 ± 50 | 0.709(3 ± 2) | 13 | 0.131 | 58–300 |
| 0.50 | 2400 ± 50 | 1.798(3 ± 2) | 38 | 0.116 | 86–300 |
| 0.75 | 2550 ± 50 | 2.504(9 ± 2) | 38 | 0.260 | 86–300 |
| 1.0 | 2850 ± 50 | 3.417(1 ± 2) | 39 | 0.284 | 86–300 |

[a] For the points in the temperature range indicated in the final column.

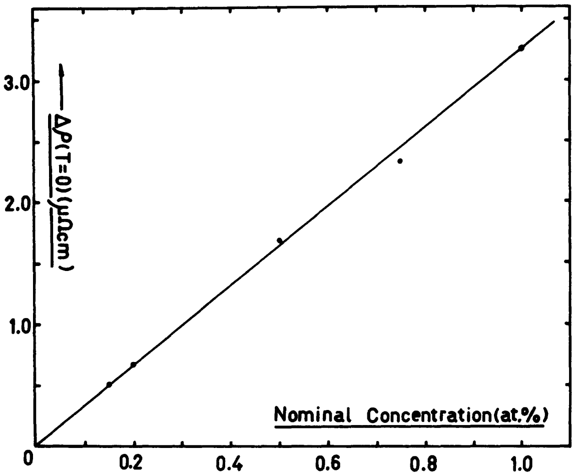

FIG. 7. $\Delta\rho(T=0)$ (in $\mu\Omega$ cm) plotted against the nominal V concentration (in at. %).

As can be seen from these figures and from the rmsd's listed in Table IV, the AK expression also provides an excellent description of the experimental data on *PdV* in the temperature region where Matthiessen's-rule breakdown does not contribute a *significant* temperature-dependent term to $\Delta\rho(T)$.[26] We emphasize that in the above fitting scheme $E$, $\delta_v$, and $T_K$ were all free parameters, *with no restriction placed on either one from alloy to alloy*. The first point of interest is that the scaling factor $E$ is linear in the nominal V concentration (see Fig. 8) as would be expected on the basis of conduction-electron scattering from essentially isolated impurities. Second, the estimated values for $T_K$ appear to be concentration independent below 0.5-at. % V, but increases as the impurity concentration is raised above this value. This we interpret as isolated V impurities having a $T_K$ of about 2300 K, with interimpurity interactions tending to quench any V moment,[9] leading to a substantial increase in $T_K$ for the interacting pair, and hence for the "average" $T_K$.

Regarding the potential phase shift $\delta_v$, in a two-band model for Pd in which the conductivity is dominated by $s$ electrons, the small values for $\delta_v$ indicate that the screening is accomplished predominantly by $d$ electrons (using the Friedel sum rule,[33] at most 0.1 charges are screened in the $s$ band). Of course, fitting $\Delta\rho(T)$ to Eq. (8) with three variable parameters means that the (small) increase in the amount of screening by $s$ electrons as the V concentration increases, indicated by the value of $\delta_v$ in Table IV, cannot be regarded as definitive.

### C. Matthiessen's-Rule Deviations

Before discussing the manner in which the Matthiessen's-rule (MR) deviations were fitted, it is necessary to indicate the manner in which these deviations were extracted from the experimental data. It is usual[23,25] to write the MR deviation $\Delta(T)$ as

$$\Delta(T)=\rho(T)-\rho_h(T)-\rho_i(T) \quad . \tag{9}$$

$\rho(T)$ is the measured resistivity of the alloy, $\rho_h(T)$ is the host's resistivity while $\rho_i(T)$ is that due to the impurities (and may[23] or may not[25] be temperature dependent). For the *PdV* alloys examined here, estimates of $\rho(T)$ were initially complicated owing to the fact that $\rho_i(T)$ was not known. However, having fitted the high-temperature data to Eq. (8),[34] the *calculated* values $\rho_i^c(T)$ for the impurity resistivity at temperatures below 80 K were obtainable from this equation, and $\Delta(T)$ taken essentially as the difference between this calculation and the measured value of the incremental resistivity $\Delta\rho(T)$:

$$\Delta(T)=[\rho_i^c(T=0)-\rho_i^c(T)]+[\Delta\rho(T)-\Delta\rho(T=0)] \quad . \tag{10}$$

The disadvantage of this approach is obvious, $\Delta(T>80\text{ K})$ becomes independent of temperature

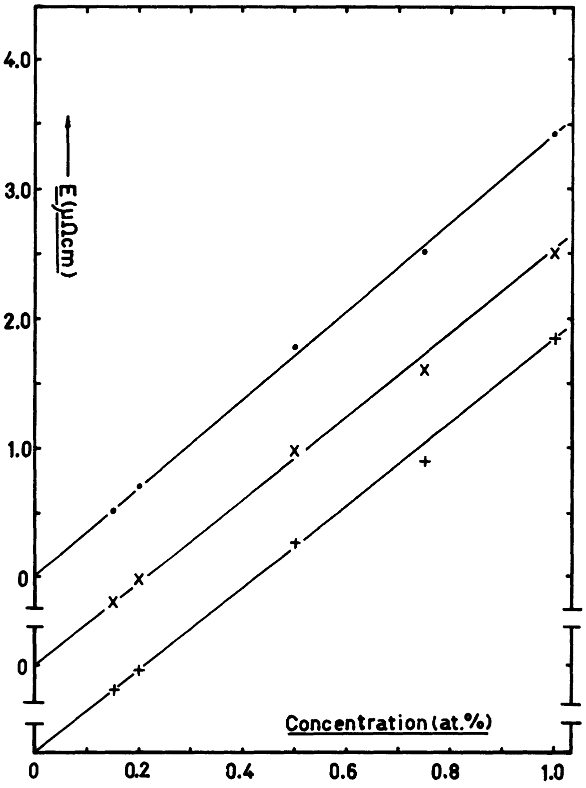

FIG. 8. Various estimates for the scaling parameter $E$ plotted against the impurity concentration $c$ (in at. %): closed circles, $E$; crosses, $E(1-\beta)$; plus signs, $E-\Delta(T>80\text{ K})$.

[as $\rho_i^c(T > 80\text{ K}) = \Delta\rho(T > 80\text{ K})$] whereas in the "parallel-conduction" model[25] used below this should only occur if $\rho_i(T)$ is *independent* of temperature. However, within the framework of this same model such an approximation cannot alter the functional form of the temperature dependence of $\rho_i(T)$ in the high-temperature region, but merely changes its magnitude. Further, the following analysis shows that this change in magnitude is only of the order of a few percent, in agreement with previous estimates for noble metal hosts.[25]

When the phonon and impurity scattering have differing wave vector dependences, the deviation $\Delta(T)$ can be written in the form[35]:

$$\frac{1}{\Delta(T)} = \frac{1}{\alpha\rho_h(T)} + \frac{1}{\beta\rho_i(T)} \tag{11}$$

with the coefficients $\alpha$ and $\beta$ usually taken to be independent of temperature, and determined by fitting the experimental data. In Fig. 9 estimates of $\Delta(T)$ from the experimental data, using Eq. (10), are plotted against temperature up to 300 K for the five alloys examined. The full lines in this figure represent the calculated deviations $\Delta(T)$ obtained from Eq. (11) [with $\rho_i(T)$ replaced by $\rho_i^c(T)$] using the values of $\alpha$ and $\beta$ listed in Table V. From these listed values it can be seen that $\alpha$ is nearly concentration independent for the alloys examined here, having a value $0.31 \pm 0.04$; this coefficient was also found to be largely concentration independent in various noble metal alloys,[23] with a value there of $1.2 \pm 0.1$. The magnitude of the term $\alpha\rho_h(T)$ however, particularly at high temperatures, is comparable in both systems. The listed values for $\beta$ (this coefficient determines the high-temperature value for $\Delta$) in *Pd*V at first increases, but then decreases with increasing impurity concentration, whereas in noble metal alloys of comparable residual resistivity $\beta$ *decreased* with increasing concentration (although the magnitudes for $\beta$ in the two systems are again comparable). A complete explanation of such variations, however, must await a comprehensive treatment of MR breakdown—an area which is currently far from well understood.

TABLE V. Values for the parameters $\alpha$ and $\beta$ in Eq. (11).

| Alloy (at.% V) | $\alpha$ | $\beta$ |
|---|---|---|
| 0.15 | 0.34 | 0.03 |
| 0.2 | 0.27 | 0.07 |
| 0.5 | 0.27 | 0.07 |
| 0.75 | 0.35 | 0.09 |
| 1.0 | 0.33 | 0.05 |

Having obtained estimates for the coefficient $\beta$ and the high-temperature deviation $\Delta(T > 80\text{ K})$, one can attempt various "corrections" to the scaling parameter $E$ [derived from fitting Eq. (8)] in an effort to account for MR breakdown. This is done in Fig. 8 in which $E$, $E(1-\beta)$, and $E - \Delta(T > 80\text{ K})$ are plotted against the nominal V concentration. While such corrections change the magnitude of $E$, they do not modify its linear concentration dependence, and so the conclusions reached in Sec. III B remain valid.

## IV. SUMMARY

The high-temperature incremental resistivity, $\Delta\rho(T > 80\text{ K})$, of several dilute *Pd*V alloys has been shown to contain a temperature-dependent contribution, which can be fitted (to high accuracy) by either a spin-fluctuation model or by the Appel-

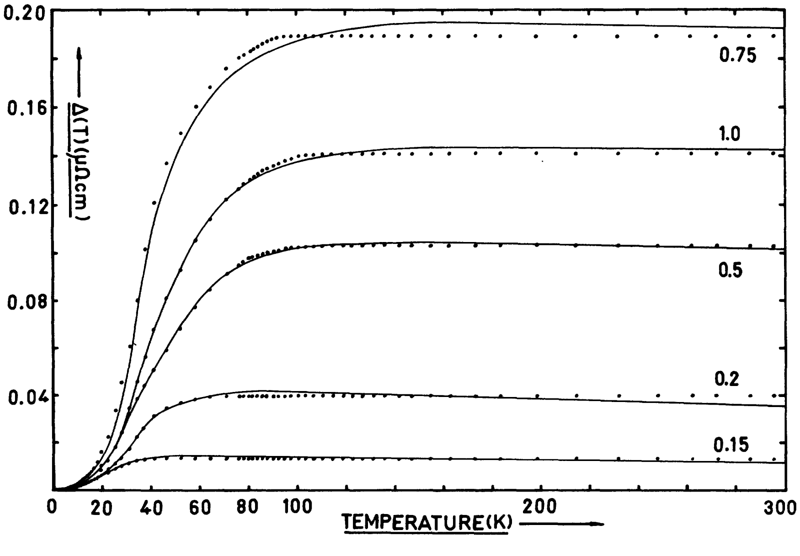

FIG. 9. Estimates of Matthiessen's-rule deviations $\Delta(T)$ (in $\mu\Omega$ cm) plotted against temperature, for the five *Pd*V alloys examined. The full lines represent calculations based on Eq. (11). The V content (in at.%) is shown next to each curve.

baum–Kondo expression. In terms of the former model, the lsf temperature $T_s$ for isolated impurities is estimated at about 160 K, while the measured change $\Delta\rho(T=0)-\Delta\rho(T\gg T_s)$ agrees in sign and magnitude with the recent predictions of a phase shift model. Various parameters, however, characteristic of the lsf model do not scale linearly with impurity concentration, and it is necessary to postulate that interimpurity interactions significantly raise $T_s$ for the interacting "pair" if this concentration dependence is to be reproduced. Using the Appelbaum–Kondo model, the Kondo temperature $T_K$ is estimated at about 2300 K; in addition the relevant parameters in this model scale linearly with impurity content. Clearly further experiments are necessary to determine the applicability of either model to this system.

Estimates have also been made of the deviations from Matthiessen's rule which contribute a significant temperature-dependent term to $\Delta\rho(T)$ below 80 K. These deviations have been fitted using a "parallel-conduction" model.

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[26] In fact, in terms of the "parallel-conduction" model of Ref. 25, this statement is only strictly true when the impurity resistivity exhibits no temperature dependence. However, in view of the slow variation with temperatures of the impurity resistivity, coupled with the small values for $\beta$ (see Table V), such an approximation appears reasonable.

[27] Using $n=150$ with the listed impurity concentration, then $c(1-c)^n$ are in the ratio 1:1.3:2:2.1:1.9 (with increasing concentration) in approximate agreement with the variation of $D$ as listed.

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