Matthiessen's rule breakdown in some Pt- and Pd-based alloys*

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The deviation from Matthiessen's rule in five *Pt*Ti, five *Pt*V, and five *Pd*Ti alloys, each containing between 0.1- and 1-at.% impurity, have been examined up to 300 K. These data for the Pt-based alloys are reasonably well fitted by a two-band model using a temperature-independent value of $\beta = 0.23 \pm 0.02$ (*Pt*Ti) and $\beta = 0.22 \pm 0.02$ (*Pt*V), whereas the estimated values for γ fall from around 0.7 at 20 K to 0.03 at room temperature. The anisotropy ratios α_i and α_ρ deduced from these data display a temperature variation which we find difficult to understand physically. The *Pd*Ti data are tolerably well fitted by the two-band model, although some discrepancies exist. As an alternative, the recently proposed empirical scheme of Caplin and Rizzuto is found to fit all these data well; the parameters $\rho'_0(T)$ and $Kf(T)$ deduced by fitting such data are found to display a variation with temperature similar to that observed in a wide range of alloy systems. For the *Pd*Ti system in both fitting schemes it appears that there *may* be an additional contribution to the resistivity at low temperatures.

INTRODUCTION

The results of recent investigations of the temperature-dependent electrical resistivity of Pt- and Pd-based alloys containing first-transition-series impurities can currently be understood in terms of conduction-electron scattering from localized spin fluctuations (lsf) at the impurity sites.[1-5] Available estimates[6] of the localized-spin-fluctuation characteristic temperature T_{sf} indicate that this quantity is low ($\ll$1K) at the center of the transition series (Mn), but increases rapidly as one moves towards either end (V, $T_{sf} > 10^2$ K; Ni, $T_{sf} \sim 10^2$ K). Such a variation is reminiscent of that followed by the Kondo temperature T_K for the same impurities in noble-metal hosts.[7] In order to estimate such parameters as T_{sf} it is frequently necessary to compare the temperature dependence exhibited by the incremental resistivity

$$\Delta\rho(T) = \rho_{\text{Alloy}}(T) - \rho_{\text{Metal}}(T) , \qquad (1)$$

with the predictions of (in this case) localized-spin-fluctuation theory in various temperature regimes [$\rho_{1sf}(T) \propto T^2$ for $T \ll T_{sf}$; $\rho_{1sf}(T) \propto \ln(T)$ for $T \gtrsim T_{sf}$, etc]. In reality however, and in particular in those systems which have rather high localized-spin-fluctuation temperatures ($T_{sf} \sim 10^2$ K) so that substantial temperature-dependent localized-spin-fluctuation scattering only occurs well above the liquid-helium range, comparisons of theoretical predictions with values of $\Delta\rho(T)$ obtained from Eq. (1) are not permissible since various contributions to the total resistivity are not additive; viz., Matthiessen's rule[8] is not, in general, obeyed. The incremental resistivity $\Delta\rho(T)$ thus contains not only $\rho_{1sf}(T)$ but also a temperature-dependent (conventional) deviation from Matthiessen's rule.

While conventional deviations have been extensively studied[9,10] in alloys based on monovalent alkali and noble metals, and polyvalent Mg and Al, much less effort has been expended in examining deviations in hosts with complex Fermi surfaces. Whether the latter does indeed have an important influence on deviations has recently been questioned as a result of data acquired on[11] Ga- and[12] Pt-based systems. In particular the observed deviations in several Pt-based alloys showed considerable similarity to those observed[13] in noble-metal alloys where a two-band model[14,15] had been extensively used to interpret the deviations.

With this in mind we undertook measurements of the electrical resistivity of several dilute *Pt*V, *Pt*Ti, and *Pd*Ti alloys up to 300 K. Previous measurements below 8 K on the *Pt*V system[16] had indicated a very high localized-spin-fluctuation temperature ($T_{sf} > 10^3$ K) which meant that temperature-dependent localized-spin-fluctuation scattering should be negligibly small below room temperature. Following the trend discussed in the opening paragraph, a similar situation was expected to exist in both *Pt*Ti and *Pd*Ti. Such measurements should, then, allow direct study of deviations in Pt- and Pd-based transition-metal alloys and hence afford a comparison between deviations induced by similar impurities in hosts with considerably different electronic structures.

EXPERIMENTAL DETAILS

The samples investigated here were produced by arc melting using 99.999% pure Pt and Pd wire, 99.99% pure Ti rod, and 99.95% pure V turnings (all supplied by Johnson Matthey, London). For each alloy series a master alloy containing 1-at.% Ti or V—as appropriate—was prepared and then annealed by inverting and remelting six times.

Melting losses were negligibly small. Alloys containing nominally 0.75-, 0.5-, 0.25-, and 0.1-at.% Ti or V were then made by diluting the appropriate master with pure Pt or Pd, and were similarly annealed. The alloys were cold rolled between Melinex into sheet form, from which resistance samples of approximate dimension $10 \times 0.2 \times 0.015$ cm were cut; these specimens were etched, washed, dried, and finally annealed at 650 °C for 24 h. in a vacuum of 10^{-6} Torr.

A standard four-probe dc potentiometric technique was used to measure the sample resistances; a Guildline Model No. 9770B current source referenced by a Guildline Model No. 9152T/6 emf standard (temperature stabilized to ±0.001 °C) provided a current stabilized to a few ppm to five alloys and one pure metal specimen connected in series. The sample voltages could be reproducibly measured to $\pm 10^{-8}$ V using a Tinsely Diesselhorst potentiometer and galvanometer amplifier. Sample temperatures between 4.2 and 300 K were measured using nonlinear gas thermometer techniques with an estimated accuracy of better than ±0.5%; temperature *differences* between the various samples, which could lead to substantial spurious contributions to $\Delta\rho(T)$ particularly at high temperatures, were minimized by clamping the specimens onto a block of high thermal conductivity Cu and surrounding them with He exchange gas. In this way temperature differences between the samples were not expected to exceed a few millidegrees over the entire range examined.

In order to extract reliable estimates of the incremental resisitivity $\Delta\rho(T)$, accurate estimates of the area to length ratio for the various samples must be made; even small errors in this quantity can lead to substantial uncertainties in $\Delta\rho(T)$ at high temperatures.[17] The area to length ratios of the samples examined here were determined to better than 0.5% using a previously described technique.[13] To assist in geometrical factor determinations, x-ray diffraction measurements were performed on the Pd-1-at.%-Ti sample using a single crystal rotation camera. These revealed an fcc structure with lattice constant 3.8902 Å, about 0.01% smaller than that for pure Pd.

RESULTS AND DISCUSSION

Pure-Pt resistivity

The pure Pt used in this investigation had an ice point resistivity of 9.80 ± 0.05 $\mu\Omega$ cm, and a resistance ratio of 2023. At temperatures below 15 K we find that the pure-Pt resistivity is well represented:

$$\rho(T) - \rho_0 = AT^2 + BT^5, \tag{2}$$

with $\rho_0 = 0.005$ $\mu\Omega$ cm; $A = 15 \times 10^{-6}$ $\mu\Omega\,\mathrm{cm/K^2}$ and $B = 13 \times 10^{-9}$ $\mu\Omega\,\mathrm{cm/K^5}$.

Alloy resistivities

In Figs. 1–3 we summarize the estimated $\Delta\rho(T)$ over the whole temperature range (4.2 to 300 K) for all the *Pt*V, *Pt*Ti, and *Pd*Ti alloys examined. The error bars used in these and subsequent figures correspond to an uncertainty of ±0.5% in the absolute resistivity, a figure which we regard as typical for the alloys investigated here.[18]

Deviations are frequently discussed using an empirically defined parameter $\Delta(T)$ given by

$$\Delta(T) = \rho_A(T) - \rho_p(T) - \rho_0\,, \tag{3}$$

where $\rho_A(T)$ is the measured alloy resistivity, $\rho_p(T)$ is the "ideal" host resistivity, and ρ_0 is the residual alloy resistivity $[\rho_0 = \rho_A(T \to 0)]$. The most obvious factor emerging from Figs. 1–3 [in which $\Delta(T) + \rho_0$ is plotted against temperature] is the similarity in both shape and magnitude[19] between the deviations observed here and that reported for a wide range of both transitional and nontransitional impurities in noble metals.[9] Such a similarity has prompted us to attempt two fitting schemes for these data; the first is the widely

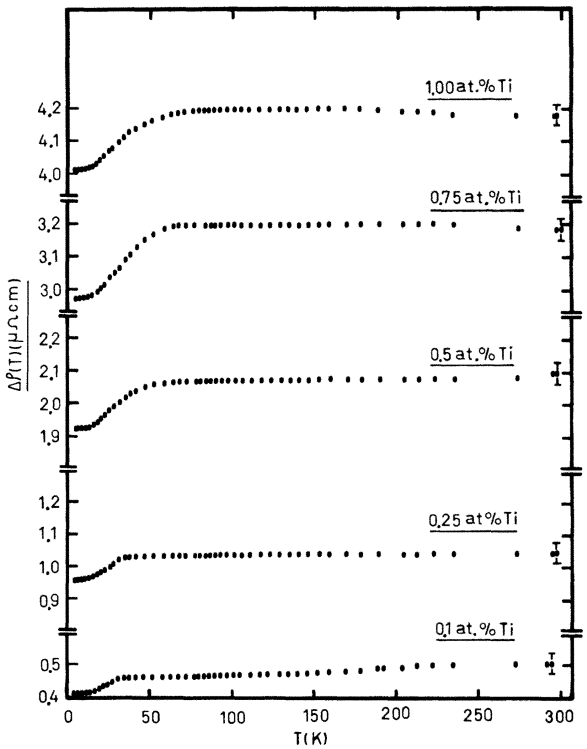

FIG. 1. Incremental resistivity $\Delta\rho(T) = \rho_{\mathrm{Alloy}}(T) - \rho_{\mathrm{Pt}}(T)$ (in $\mu\Omega$cm) plotted against temperature (in K) up to 300 K for the *Pt*Ti alloys.

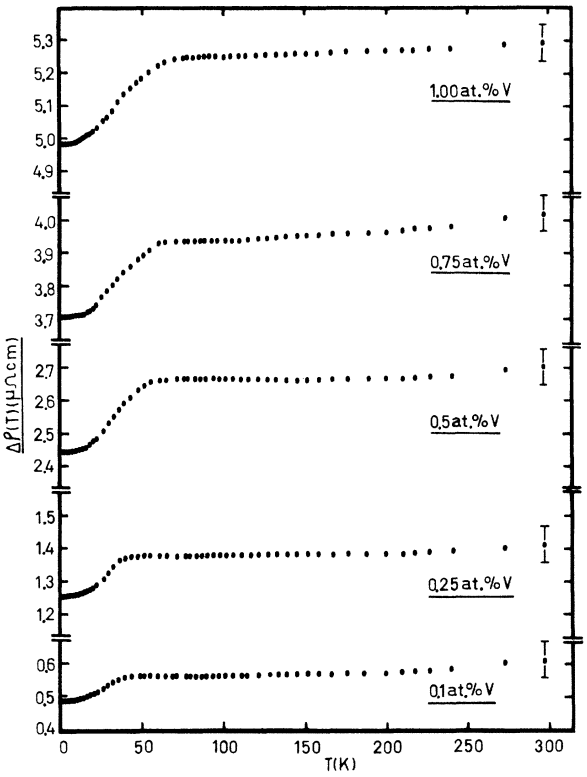

FIG. 2. Incremental resistivity $\Delta\rho(T)=\rho_{\text{Alloy}}(T)-\rho_{\text{Pt}}(T)$ (in $\mu\Omega$cm) plotted against temperature (in K) up to 300 K for the *Pt*V alloys.

quoted two-band model which we use since its form appears capable of reproducing the deviations observed here. The physical basis of this model, however, in metals with complicated Fermi surfaces is currently not clear. In addition it appears that since this approach is capable of reproducing the observed deviations in both simple and complex hosts, its interpretation in the former systems has some doubts associated with it. The second fitting scheme attempted is the recently suggested empirical formula of Caplin and Ruzzuto,[20] discussed in detail by Cimberle *et al.*[10]

1. Two-band model

The two-band model[13-15] provides the following expression for $\Delta(T)$:

$$\Delta(T)=\gamma\beta\rho_p(T)\rho_0/[\gamma\rho_p(T)+\beta\rho_0], \tag{4}$$

where γ and β are usually regarded as parameters to be determined from experimental data, and may be temperature dependent. Within the framework of this model γ and β are given by

$$\gamma=\frac{1}{\alpha_p}\left(\frac{\alpha_p-\alpha_i}{1+\alpha_i}\right)^2, \tag{5}$$

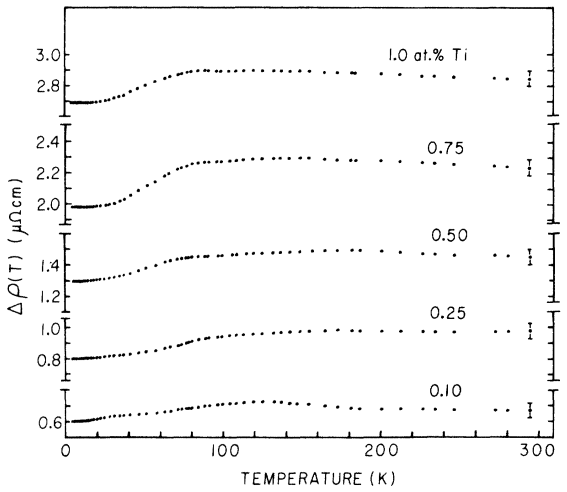

FIG. 3. Incremental resistivity $\Delta\rho(T)=\rho_A(T)-\rho_{\text{Pd}}(T)$ (in $\mu\Omega$cm) plotted against temperature (in K) up to 300 K for the *Pd*Ti alloys.

$$\beta=\frac{1}{\alpha_i}\left(\frac{\alpha_p-\alpha_i}{1+\alpha_p}\right)^2, \tag{6}$$

while

$$\alpha_p=\left(\frac{\sigma_1}{\sigma_2}\right)_{\text{phonons}} \quad \text{and} \quad \alpha_i=\left(\frac{\sigma_1}{\sigma_2}\right)_{\text{impurities}}, \tag{7}$$

the ratios of the conductivities of the "two sets of carriers" due to phonon scattering alone and impurity scattering alone.

Experimentally, the predictions of the two-band model can be tested by plotting $\Delta(T)^{-1}$ against ρ_0^{-1} at various fixed temperatures. According to Eq. (4) such a plot should result in a straight line with slope β^{-1} and y intercept $[\gamma\rho_p(T)]^{-1}$. Typical plots of this kind for the *Pt*-based alloys are reproduced in Fig. 4 and demonstrate that Eq. (4) does indeed give a reasonable representation of the deviations reported here; such figures enable γ and β to be estimated at various fixed temperatures. Within experimental error we find β to be independent of temperature in both the *Pt*Ti and *Pt*V systems with a value of 0.23 ± 0.02 in *Pt*Ti and 0.22 ± 0.02 in *Pt*V; these estimates for β are close to the value derived for this parameter for first transition series impurities in Au,[13] where β was also found to be temperature independent. The values deduced for γ, however, are temperature dependent, decreasing in both systems from a value of ~0.7 at 20 K to about 0.03 at room temperature, as indicated in Fig. 5. This decrease in γ with increasing temperature again parallels the behavior found in Au based alloys with first transition series impurities,[13] but the absolute values for γ obtained here are typically 40% lower.

It would appear then that the deviations in *Pt*Ti

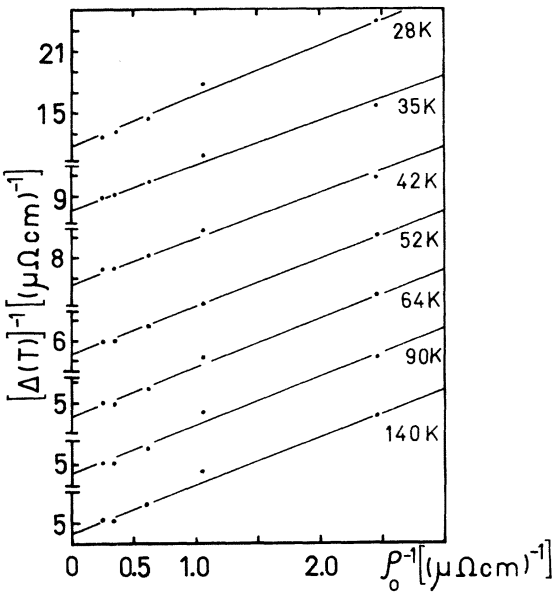

FIG. 4. Plots of $[\Delta(T)]^{-1}$[in $(\mu\Omega cm)^{-1}$] against ρ_0^{-1} [in $(\mu\Omega cm)^{-1}$] for the *Pt*V alloys at various fixed temperatures.

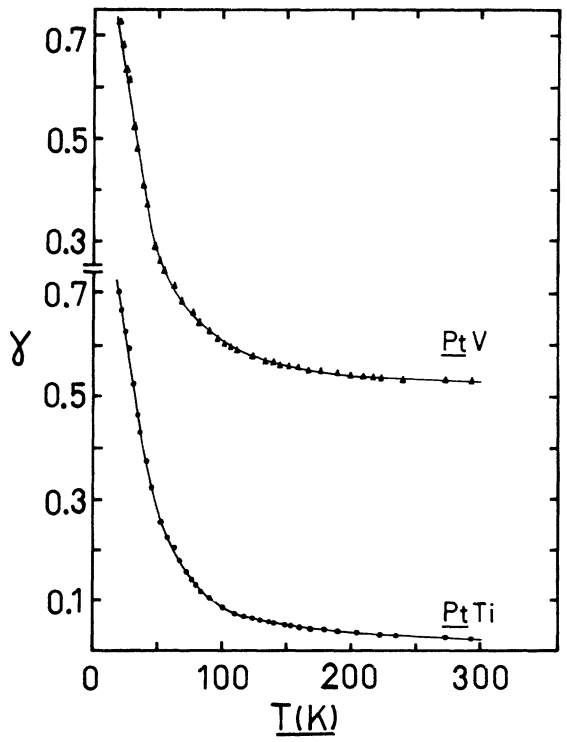

FIG. 5. Values of γ derived from plots such as those in Fig. 4, plotted against temperature (in K) up to 300 K for the *Pt*Ti and *Pt*V systems.

and *Pt*V reported here can be accounted for within the framework of a two-band model in which β is temperature independent but γ is a decreasing function of temperature.

This two-band approach can be pursued further by using the estimated values for γ and β to find α_i and α_p. Inverting Eqs. (5) and (6) yields[12]

$$\alpha_i = 1 + \tfrac{1}{2}a \pm \tfrac{1}{2}a\,(1+4/a)^{1/2}\,, \tag{8}$$

$$\alpha_p = 1 + \tfrac{1}{2}b \pm \tfrac{1}{2}b\,(1+4/b)^{1/2}\,, \tag{9}$$

where

$$a = \frac{(\gamma - \beta - \beta\gamma)^2}{\beta\gamma^2} \quad \text{and} \quad b = \frac{(\beta - \gamma - \beta\gamma)^2}{\beta^2\gamma}\,. \tag{10}$$

The use of one sign in Eqs. (8) and (9) will give the ratio (σ_1/σ_2) for the appropriate scattering agent, while the other sign gives the inverse ratio (σ_2/σ_1). However, for self-consistency, if one sign is chosen in (8), the other should be chosen[21] in (9). In Fig. 6 we reproduce estimates of α_i and α_p obtained at various fixed temperatures for both the *Pt*Ti and *Pt*V systems. From this figure it can be seen that α_i, the anisotropy of the impurity scattering, decreases slightly and then increases monotonically with increasing temperature which, in a two-band sense, would mean a strong impurity scattering of one type of carrier evolving as the temperature increases. For the case of α_p, as the temperature is increased from the low-temperature regime, α_p climbs towards a value of unity (such an increase has frequently been attributed to phonon scattering becoming increasingly isotropic as the temperature increases), however as the temperature is increased still further α_p ceases to increase and begins to decrease with increasing temperature, this

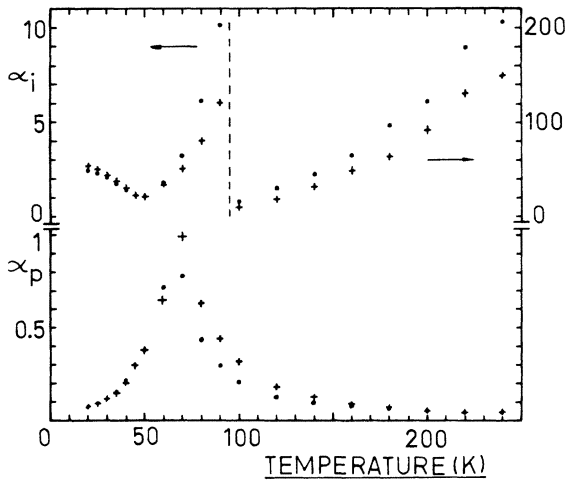

FIG. 6. Estimates of the anisotropy parameters α_i and α_p (obtained in the manner described in the text) plotted against temperature; (●) *Pt*Ti; (+) *Pt*V.

decrease continuing up to room temperature. We note that both the change in sign of the temperature derivative of α_p and α_i occurs in the region of transition from $\gamma > \beta$ to $\beta > \gamma$. Such changes are a property of the two band model as expressed via Eqs. (8) and (9) *and will always occur, irrespective of the alloy system being studied* as one passes from $\gamma > \beta$ to $\beta > \gamma$ (at least for $\beta < 1$).

This result casts further doubt on the physical basis of the two-band model, since even in noble-metal-based alloys if the decrease in γ evident[13] below 60 K persists to higher temperatures, then a transition from $\gamma > \beta$ to $\beta > \gamma$ will occur, and the temperature derivative of α_p will be reversed. Thus the phonon scattering, initially assumed to become increasingly isotropic as the temperature increases, must now revert to becoming increasingly anisotropic as the temperature is increased still further. The physical basis for such an effect is not clear.

In Fig. 7 we reproduce plots of $[\Delta(T)]^{-1}$ against ρ_0^{-1} for the *Pd*Ti alloys, between 35 and 140 K. From this figure it can be seen that the two band predictions fit these data quite well at the lower end of this temperature range, but the quality of the fit deteriorates with increasing temperature. Similar plots above 140 K exhibit comparable scatter to those shown at 140 K. In Fig. 8 the values for γ and β deduced from such plots are displayed as a function of temperature. The dashed lines in this figure indicate those regions where there is some uncertainty in the values deduced for γ and β; these fall into two temperature ranges: (i) at higher temperatures, as mentioned above, the prediction of the two-band model [viz., a linear relationship between $\Delta(T)^{-1}$ and ρ_0^{-1} at fixed temperature] is not convincingly obeyed; (ii) closer examination of the data below 40 K reveals that the magnitude of $\Delta(T)$ at such temperatures is substantially less than that found in *Pt*Ti and *Pt*V. These smaller values for $\Delta(T)$, particularly below 25 K, mean that small errors in $\Delta(T)$ lead to a large spread in $\Delta(T)^{-1}$, with consequent uncertainties in β and γ deduced from $\Delta(T)^{-1}$-vs-ρ_0^{-1} plots. In spite of these difficulties it is still clear from Fig. 7 that in the *Pd*Ti system the observed deviations can be fitted by a two-band model only if both γ and β are allowed to vary with temperature. This result then contrasts with that inferred from the *Pt*Ti and *Pt*V data, where a temperature-independent value for β was obtained. More specifically, the maximum value for β in the *Pd*Ti system (0.27) is close to the temperature-independent value (0.23) found in the Pt-based systems. The variation of γ with temperature resembles that found in the *Pt*Ti and *Pt*V systems at high temperatures,

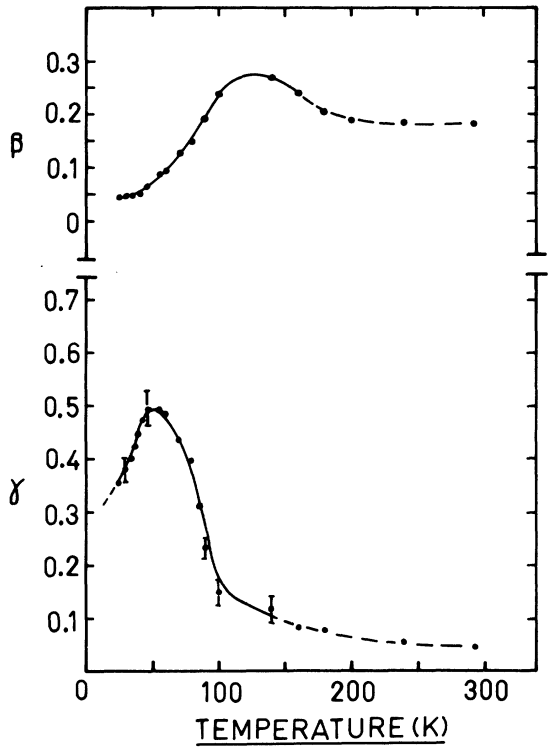

FIG. 8. Values for γ and β deduced from plots such as those in Fig. 7, plotted against temperature (in K) up to 300 K. The dashed portions indicate regions of some uncertainty.

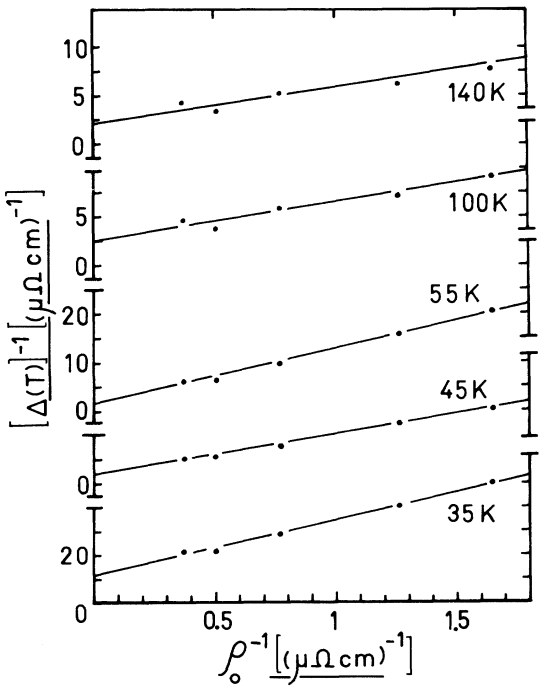

FIG. 7. Plots of $[\Delta(T)]^{-1}$[in $(\mu\Omega\,\mathrm{cm})^{-1}$] against ρ_0^{-1} [in $\mu\Omega\,\mathrm{cm})^{-1}$] at various fixed temperatures.

viz., γ increases with decreasing temperature. However, in the present system γ exhibits a maximum around 50 K, a feature not observed in the Pt-based systems where γ increased monotonically with decreasing temperature. This decrease in both β and γ below 50 K has led us to suspect that there *may* be an additional source of scattering present in the *Pd*Ti system, whose contribution decreases with increasing temperature (possibly associated with internal degrees of freedom at the Ti impurity sites); direct evidence for such an effect is however clearly lacking.

Having obtained estimates for γ and β at various temperatures it is then possible to deduce values for

$$\alpha_p = \left(\frac{\sigma_1}{\sigma_2}\right)_{\text{phonons}} \quad \text{and} \quad \alpha_i = \left(\frac{\sigma_1}{\sigma_2}\right)_{\text{impurities}} .$$

The estimates obtained for α_i and α_p using the values of γ and β shown in Fig. 8 exhibit much the same behavior as those deduced for the Pt-based alloys, and hence are not tabulated here. In particular, in the region of transition from $\gamma > \beta$ to $\beta > \gamma$ (around 90 K in the present system), the temperature derivative of α_p changes sign (from positive to negative), with the result that the phonon scattering appears to become progressively more *anisotropic* above 90 K. This behavior mirrors that already reported for the Pt-based alloys, and in both systems the physical origin for such an effect is not obvious; from this we infer that further doubt has been thrown onto the validity of the two-band approach.

2. *Empirical model*

The above model,[20] recently discussed in detail by Cimberle *et al.*,[10] uses the following relationships:

$$\rho_A(T) - \rho_0 = \rho_p(T) \quad \text{for } \rho_0 < \rho_0'(T) \tag{11}$$

and

$$\rho_A(T) - \rho_0 = \rho_p(T) + Kf(T)\log_{10}\left(\frac{\rho_0}{\rho_0'(T)}\right) \quad \text{for } \rho_0 > \rho_0'(T) . \tag{12}$$

Equations (11) and (12) imply two differing types of behavior above and below some well-defined value of the residual resistivity, although the value of ρ_0 which defines the boundaries of the two regions is temperature dependent $[\rho_0'(T)]$. Below $\rho_0'(T)$ Matthiessen's rule is valid, above $\rho_0'(T)$ it is not. The validity of Eqs. (11) and (12) for Pt-based alloys has been demonstrated only for a small number of alloys[10] over a temperature range <50 K. In Fig. 9 we indicate the applicability of this empirical approach to the *Pt*Ti and *Pt*V systems at temperatures between 10 and 50 K. (The data between 50 and 273 K are very similar to the plot shown for the 50-K data.) Again the error bars in these figures correspond to an uncertainty of ±0.5% in the absolute resistivities, which, because of the large values for $\rho_p(T)$ in these systems, translates into an absolute error in $\rho_A(T) - \rho_0$ up to a factor of 5 larger than in the corresponding noble-metal-based systems.

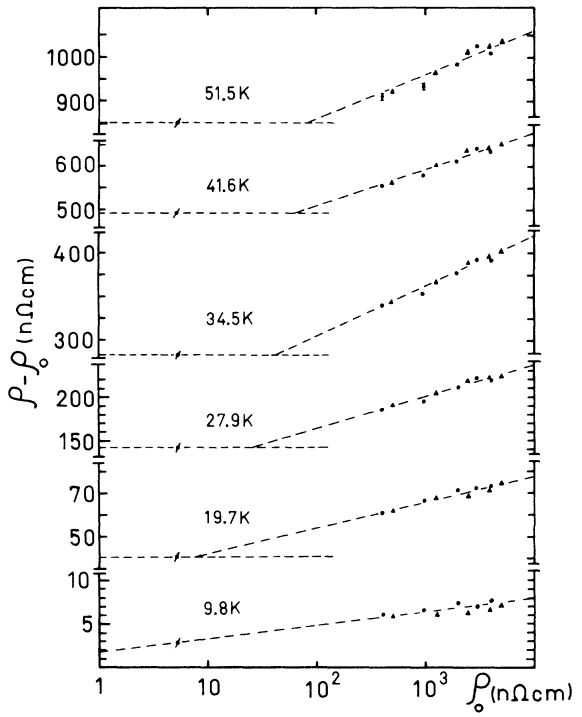

FIG. 9. Plots of $\rho_{\text{Alloy}}(T) - \rho_0$ (in $n\Omega$ cm) against $\log_{10}\rho_0$ for the *Pt*Ti and *Pt*V alloys at various fixed temperatures between 10 and 52 K.

In Fig. 10 we plot the estimates of $\rho_0'(T)$ against

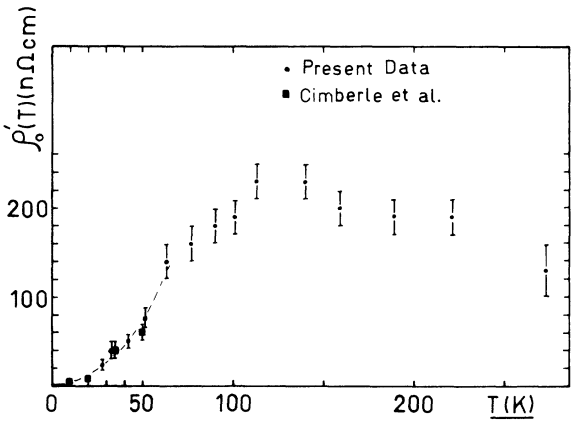

FIG. 10. Breakdown residual resistivity $\rho_0'(T)$ (in $n\Omega$ cm) derived as explained in the text, plotted against temperature (in K) up to 273 K.

temperature, up to 273 K. At low temperatures ($T<50$ K), our values for $\rho_0'(T)$ agree with those previously reported[10]; further, the general shape of the $\rho_0'(T)$-vs-T plot is similar to that for Cu, the only other host to have been examined over a comparable temperature interval. Finally, in Fig. 11, we plot the function $Kf(T)$ estimated at 16 different temperatures from the data similar to that in Fig. 9, against T/Θ_D (with the Debye temperature[22] $\Theta_D = 240$ K). Over the temperature range 10–35 K this function is found to be proportional to T^n with $n = 3.2 \pm 0.3$, in excellent agreement with that found by Cimberle *et al.* from an analysis of the existing data over the same temperature range.

We were initially hesitant about fitting the *Pd*Ti data to the empirical scheme, owing to our suspicion that there may be an additional impurity contributed term in $\rho_A(T)$. If this were so it would lead to values of $\rho_A(T) - \rho_0$ lower than the "proper" values for Pd-based alloys, as has been observed[4] for Rh impurities in Pt, but unlike the situation in Pt alloys, with no available information on deviations in Pd, there exists no means for comparison from which such a reduction could be detected. It should be noted however that since Eq. (12) calls for a $[\rho_A(T) - \rho_0]$-vs-$\log_{10}\rho_0$ plot, then the predominant effect of a reduction in $\rho_A(T) - \rho_0$ from an anomalous impurity contribution should show up in the form of an increased value for $\rho_0'(T)$ rather than in changes in $Kf(T)$.

In Fig. 12 the *Pd*Ti data are plotted in the form $\rho_A(T) - \rho_0$ vs $\log_{10}\rho_0$ at various fixed temperatures between 25 and 63 K; the error bars in these figures correspond to an uncertainty of ±0.5% in the absolute resistivities, and arises predominantly from shape factor limitations. Owing to the large values for $\rho_p(T)$ in Pd this uncertainty translates into a substantially larger error in $\rho_A(T) - \rho_0$ compared with, typically, noble-metal-based alloys.

In Fig. 13 the estimated values for $\rho_0'(T)$ are plotted against temperature, up to 273 K. As with most other systems examined,[10] $\rho_0'(T)$ can be seen to increase as T^2 below 50 K—as indicated by the dashed curve. Above 100 K $\rho_0'(T)$ appears to flatten off to an approximately temperature-independent value, as has been observed in Cu,[10] and Pt, the only other hosts to have been investigated at these higher temperatures. In the low-temperature region however, the absolute values for $\rho_0'(T)$ estimated for the *Pd*Ti system are the highest so far reported, being more than three times larger than those estimated for Pt based alloys (a host with similar electronic structure) at comparable temperatures. As mentioned previously, large values for $\rho_0'(T)$ could be indicative of an anomalous impurity contribution in the resistivity.

The function $Kf(T)$, estimated at 15 different temperatures between 25 and 273 K, is displayed as a function of T/Θ_D (with the Debye temperature Θ_D taken as[22] 274 K) in Fig. 14. Again, in this

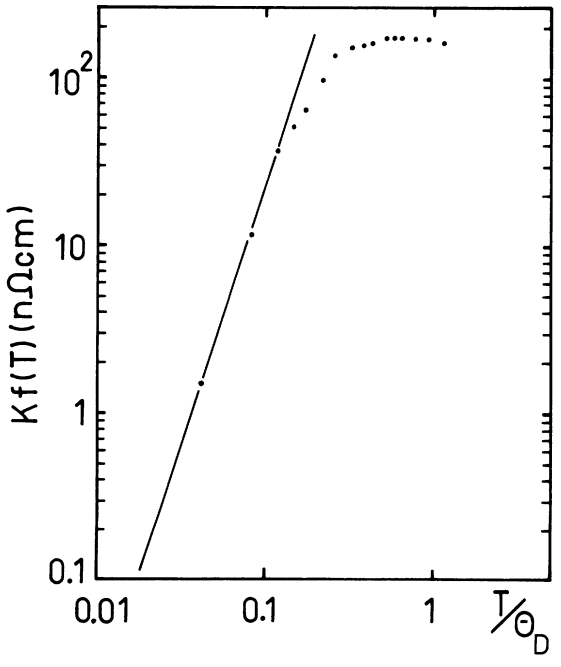

FIG. 11. Function $Kf(T)$ (in $n\Omega$ cm) derived from the plots similar to those shown in Fig. 9, plotted against T/θ_D. The line drawn at low temperatures has a slope of 3.2 ± 0.3.

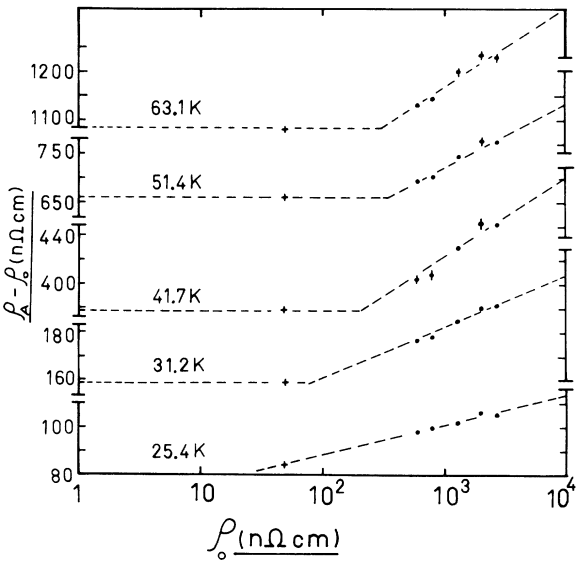

FIG. 12. Plots of $\rho_A(T) - \rho_0$ (in $n\Omega$ cm) against $\log_{10}\rho_0$ at various fixed temperatures between 25 and 63 K.

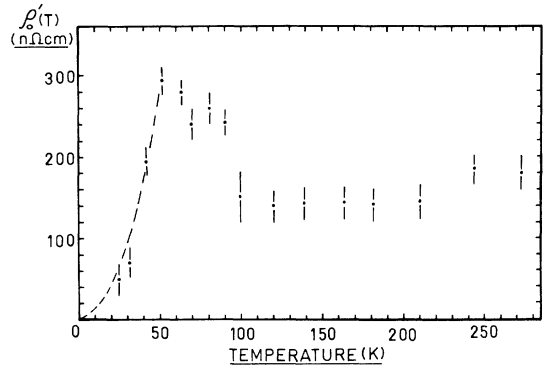

FIG. 13. Estimated breakdown resistivity $\rho_0'(T)$ (in $n\Omega$ cm) deduced from Fig. 12, plotted against temperature (in K) up to 273 K. The dashed curve indicates an initial parabolic dependence.

system $Kf(T)$ exhibits much the same variation with reduced temperature as it does in both Cu (Ref. 10) and Pt; at low temperatures $Kf(T)$ can be seen to be proportional to T^n with $n = 3.3 \pm 0.3$, in excellent agreement with the value for this exponent derived from data[10] on Pt-, Au-, and Ag-based alloys. At higher temperatures the estimated values for $Kf(T)$ level off to an approximately temperature-independent plateau, as in Cu and Pt. While the variation with reduced temperatures is much the same as that reported for other metals, the absolute values for $Kf(T)$ are the largest so far reported; however, since there appears to be a direct correlation between the magnitudes of $Kf(T)$ and $\rho_0'(T)$, this result could simply reflect the large estimated values for $\rho_0'(T)$ in this system, which were discussed above.

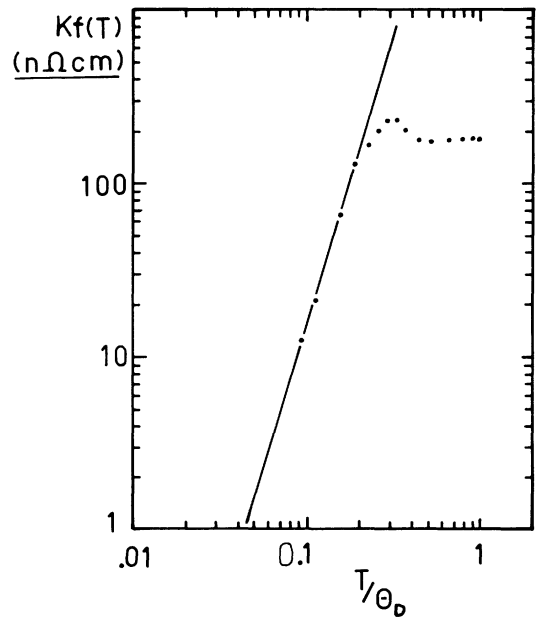

FIG. 14. Function $Kf(T)$ (in $n\Omega$ cm) for PdTi derived from plots similar to those in Fig. 12, plotted against T/θ_D. The line drawn at low temperatures has a slope of 3.3 ± 0.3.

To conclude, it appears that the empirical model is capable of providing a good representation of the deviations in the PdTi system. The parameters deduced from this empirical scheme display a variation with temperature which is in good agreement with that observed in a wide variety of alloy systems, however the magnitudes associated with both $\rho_0'(T)$ and $Kf(T)$ are the largest yet reported. We feel that this latter result *may* have its origin in an anomalous impurity contributed resistivity, although direct observation of this effect has not been possible.

SUMMARY

We have examined the deviations up to 300 K in ten PtTi and PtV alloys containing between 0.1- and 1-at.% impurity. These deviations can be reasonably well fitted by a two-band model which uses a temperature-independent value for $\beta \simeq 0.2$ in both systems, whereas the estimated values for γ fall smoothly from ~0.7 at 20 K to 0.03 to room temperature. However values of the anisotropy ratios α_i and α_p deduced from these values of β and γ display a variation with temperature which is difficult to appreciate physically, and from which we infer that further doubt is cast on physical basis of this model.

The deviations in five PdTi alloys have been examined over the same temperature range. Between 35 and 140 K these data can also be fitted using the predictions of a two-band model, but a temperature-dependent γ and β must be used; outside this temperature range some discrepancies exist.

These data are also well fitted by a recently proposed empirical scheme, with the parameters derived from such a scheme displaying characteristics similar to those established in a wide range of alloy systems. This empirical scheme, however, also awaits a firm theoretical foundation.

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Financial support from the National Research Council of Canada and the Research Board of the University of Manitoba are also acknowledged.

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[18]Shape factor uncertainties we estimate to be better than ±0.5%, however there are several other corrections. (i) Thermally induced changes in the geometrical shape factor (which depends on the thermal expansion). From the available data on Pt this correction is estimated at $< 0.015\ \mu\Omega$cm at 300K. (ii) Temperature-dependent changes in the residual resistivity induced by thermal variations in the atomic volume. Such effects are related not only to the thermal expansion but also to the volume dependence of the residual resistivity. (iii) Impurity induced changes in the atomic volume of the lattice could lead to an ideal resistivity in the dilated lattice different from that in the pure lattice. Such a contribution depends on both the volume dependence of the ideal resistivity and the lattice parameter changes produced by alloying. With little available information on the relevant parameters necessary for an evaluation of (ii) and (iii) in the *Pt*Ti and *Pt*V alloy systems, we are guided by available estimates for other transition metal alloy systems [see, for example, D. C. Price and Gwyn Williams, J. Phys. F 3, 810 (1973)].
[19]Specifically the ratio $\Delta(\max)/\rho_0$ decreases from 0.2 to 0.05 as the impurity content is raised from 0.1-to 1-at.% in both *Pt*Ti and *Pt*V. The same ratio decreases from 0.25 to 0.07 over the same impurity content range in *Pd*Ti.
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