distributions are normalized to the same total number of counts. Since no gross effects were observed, the investigation was discontinued in favor of other work. These preliminary results have been included here because they may be of use to other investigators. In particular, they indicate that if the angular correlation method is to be of use in the study of Pd—H alloys, rather precise measurements with good statistics will be required.

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Electrical Resistivity of the Ni—Pd Alloy System between 300°K and 730°K

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Electrical resistivity measurements have been made on alloys of Ni and Pd from room temperature to 730°K. The maximum in the resistivity was found to shift from 70 atomic percent Pd 30 atomic percent Ni at room temperature, to the 50–50 composition at temperatures where all the specimens are paramagnetic. At these elevated temperatures it was found that Matthiessen's rule is obeyed over the entire range of compositions. The general behavior may be interpreted in terms of the dependence of *s-d* scattering upon temperature and composition.

INTRODUCTION

ELECTRICAL resistivity measurements between 300°K and 730°K for the Ni—Pd alloy system will be discussed in this paper. Preliminary measurements between 4.2°K and 300°K have already been published for this system.[1] The results showed that at the low temperatures the resistivity is a maximum at 70 atomic percent Pd. This was explained by splitting up the resistivity into two parts: one, $\rho_{s\text{-}s}$, resulting from *s-s* scattering, and one, $\rho_{s\text{-}d}$, resulting from *s-d* scattering, and then considering how these parts varied with composition. Ni is ferromagnetic up to 629°K and Pd is paramagnetic at all temperatures. Both elements contain 0.6 hole in their respective *d* bands (3-*d* for Ni and 4-*d* for Pd) and 0.6 conduction electrons in the *s* bands (4-*s* for Ni and 5-*s* for Pd). It is reasonable to assume that the number of *s* electrons remains constant with composition at 0.6[2] and consequently $\rho_{s\text{-}s}$ will vary in a Nordheim manner,[3] i.e., as $x(1-x)$, where x is the fraction of Pd atoms. While the number of holes in the *d* band is 0.6 for each composition, the effective number of Bohr magnetons, calculated from magnetization data, changes from a maximum for pure Ni to zero for 97 atomic percent Pd. This implies that the filling of the two half *d* bands changes gradually with composition from Ni to Pd. Half of the *d* band for Ni is completely filled and the other half contains 0.6 hole, thus allowing electrons of only one spin state to contribute to *s-d* scattering. In Pd both halves of the *d* band are equally populated with the same number of holes, so that electrons of both spins may be scattered from *s* to *d* states.

The total resistivity has been represented by Overhauser and Schindler[4] as

$$\rho=\frac{x(1-x)(S+Dq{\uparrow}^{p})(S+Dq{\downarrow}^{p})}{2S+Dq{\uparrow}^{p}+Dq{\downarrow}^{p}}, \tag{1}$$

where x is the Pd content, $q\uparrow$ and $q\downarrow$ are the number of holes in the spin-up and spin-down portions of the *d* band respectively, S and D are terms independent of composition referring to *s-s* and *s-d* transitions and p is related to the band shape and is approximately unity. An examination of Eq. (1) reveals that since $q\uparrow$ and $q\downarrow$ are in general functions of composition, an asymmetrical variation of ρ with composition is to be expected. However, when $q\uparrow$ is equal to $q\downarrow$ and is composition-independent, then ρ varies as $x(1-x)$ and ρ is consequently symmetrical about the 50–50 composition. This is equivalent to the earlier prediction of the authors[1] that the Nordheim relation should be applicable in the region where all of the alloys are paramagnetic, i.e., above the Curie temperature of nickel.

EXPERIMENTAL PROCEDURE AND RESULTS

The resistivity measurements between 300°K and 730°K were carried out with the specimens in a vacuum. The temperature gradient did not exceed 0.25°C between the potential leads, which were approximately

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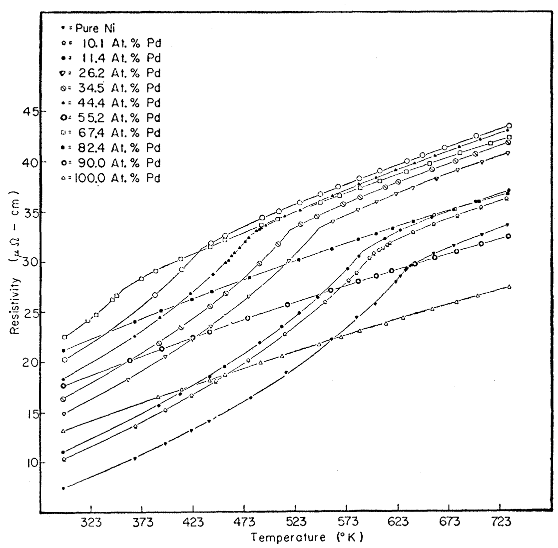

FIG. 1. Electrical resistivity *vs* temperature for Ni—Pd alloys.

8 cm apart. To keep the gradient within this limit a furnace two feet long was modified so that it held three independently variable heater elements. A copper cylinder 25 cm long with radiation reflectors at each end was used as a container for six specimens and as a heat-sink. The specimens were vacuum-annealed at 1070°K for two hours and then furnace-cooled for twenty-four hours. The measurements were made on a modified Kelvin bridge in which errors due to contact and lead resistance were minimized.

Figure 1 gives resistivity *versus* temperature between 300°K and 730°K for each of the compositions used. The Curie temperatures of these alloys may be obtained from this graph by noting where the curvature changes from positive to negative as the temperature increases. These results with those of reference 1 are plotted in Fig. 2 and compare favorably with older data.[5]

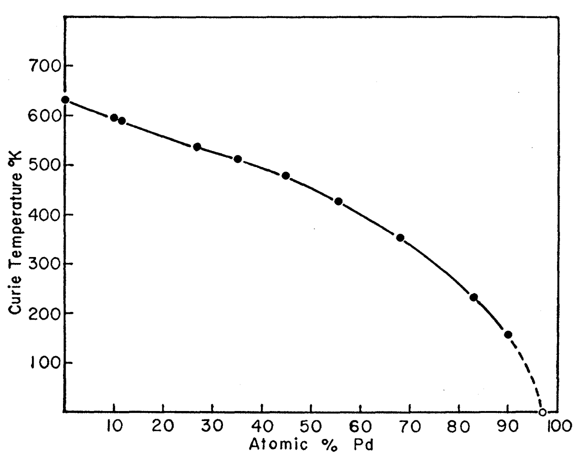

FIG. 2. Curie temperature *vs* composition for Ni—Pd alloys as obtained from resistivity measurements.

[5] V. Marian, Ann. Physik 7, 459 (1937).

Figure 3 shows ρ as a function of composition at 323°K, 373°K, 423°K, 473°K, 523°K, 623°K and 723°K. The maximum in ρ is observed to shift from approximately 70 atomic percent Pd at 323°K to 50 atomic percent Pd at 723°K. In addition, the resistivity of Ni becomes greater than the resistivity of Pd as the temperature increases.

The changes in the resistivity with respect to temperature, $d\rho/dT$, *versus* composition are found in Fig. 4, some of the data having been reported in reference 1. The curves are plotted for 4.2°K–63°K, 70°K, 300°K and 723°K, and it is observed that $d\rho/dT$ is practically constant at 723°K. The dotted portions of the curves represent regions where $d\rho/dT$ varies rapidly and the precise behavior is not known.

DISCUSSION OF RESULTS

The anticipated shift in the maximum of the ρ *versus* composition curve from approximately 70 atomic percent Pd to 50 atomic percent Pd at the higher temperatures is clearly displayed in Fig. 3.

The effect of temperature upon pure Ni is to change the distribution of the holes in the two half d bands, but does not affect the s band. It is very interesting to observe that this is precisely the effect of alloying Ni with Pd. For as Pd is added to Ni, the distribution of the holes in the two half-bands is changed but again the s band is unaltered. This can be illustrated by comparing Fig. 4 with Fig. 5. In Fig. 5, the resistivity is plotted against temperature for a ferromagnetic metal. For purposes of discussion three regions have been delineated. Region I represents the behavior of the resistivity below the Curie temperature. Here, $d\rho/dT$ increases gradually in going from A to B, and is a reflection of the change in the distribution of the d holes. In Fig. 4, curves 1 and 2 represent the behavior of $d\rho/dT$ of the Ni—Pd series as a function of Pd content at temperatures well below the Curie temperature for the available alloys. Again the gradual increase of $d\rho/dT$

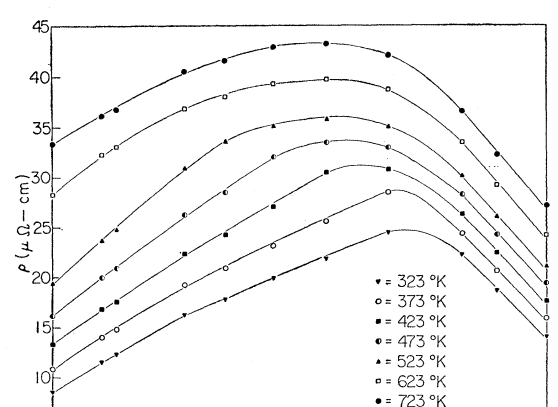

FIG. 3. Electrical resistivity *vs* composition for Ni—Pd alloys.

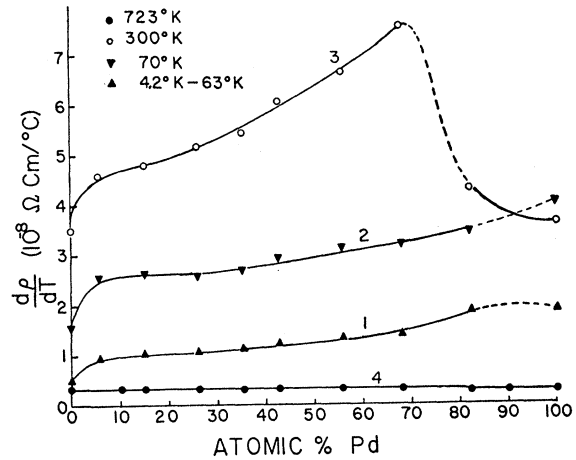

FIG. 4. $d\rho/dT$ *vs* composition for Ni–Pd alloys at various temperature.

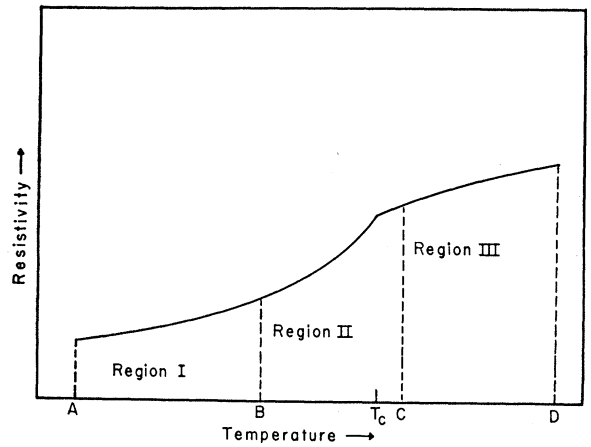

FIG. 5. Schematic plot of resistivity *vs* temperature for a ferromagnetic metal.

with increasing content reflect the change in the distribution of the d holes.

Region II of Fig. 5 displays the $d\rho/dT$ variation in the vicinity of the Curie temperature. As the Curie temperature is approached from below, $d\rho/dT$ increases rapidly, has a maximum at the Curie temperature and then decreases rapidly. This region should be compared to curve 3 of Fig. 4, where it is evident that 300°K is the Curie temperature of an alloy containing approximately 75% Pd.

Region III of Fig. 5 represents the resistivity of pure Ni, above the Curie temperature where $d\rho/dT$ changes slowly and the resistivity curve has a negative curvature. Similarly, curve 4 of Fig. 4 represents $d\rho/dT$ for the whole Ni–Pd series well above the Curie points of all the alloys and $d\rho/dT$ is found to be almost constant, decreasing very slowly with increasing Pd content.

Matthiessen's rule states that for an alloy system, $d\rho/dT$ is independent of concentration. The quantum-mechanical verification of this rule is for single-band conduction and dilute concentrations. Conduction in the transition elements is a two-band process. Since alloying Ni with Pd changes the population of the two half d bands, Matthiessen's rule should not be expected to be valid. But above 629°K, the Curie temperature of Ni, both halves of the d band for all of these alloys are equally populated, and Matthiessen's rule is obeyed over the entire range of composition (see Fig. 4).

Ni is adjacent to Cu in the periodic table and their atomic volumes are approximately the same. This indicates that the difference in the electrical resistivity of these two elements is related to the additional s-d scattering found for Ni. Following this line of reasoning for Pd and Ag, one might expect

$$\rho_{\mathrm{Ni}}/\rho_{\mathrm{Cu}} \cong \rho_{\mathrm{Pd}}/\rho_{\mathrm{Ag}}$$

in the temperature region where the s-d scattering of Ni is similar to that of Pd. Since the resistivity of Cu is greater than that of Ag, ρ_{Ni} should be greater than ρ_{Pd} when Ni is paramagnetic. At the elevated temperatures (723°K) it is indeed found that $\rho_{\mathrm{Ni}} > \rho_{\mathrm{Pd}}$, and the difference of the ratios $\rho_{\mathrm{Ni}}/\rho_{\mathrm{Cu}}$ and $\rho_{\mathrm{Pd}}/\rho_{\mathrm{Ag}}$ is less than 10%. However, at 300°K, where Ni is still ferromagnetic, ρ_{Pd} is almost twice ρ_{Ni}.

CONCLUSION

It has been demostrated that the asymmetry associated with the resistivity *versus* composition curves for the Ni–Pd system at the low temperatures results from the composition dependence of the filling of the two half d bands. At the elevated temperatures, when the two halves of the d band. are equally filled and composition independent, the Nordheim relation is obeyed. Matthiessen's rule is also obeyed at the elevated temperatures over the entire range of composition.*

* *Note added in proof.*—The variation with composition of ρ_T, the phonon contribution to the resistivity, can be easily calculated for these alloys using the data presented here and that of reference 1. This variation should be related to the variation with energy of the density of states of the d band. Because of the complications arising from the spin dependence of the scattering upon ρ_T, this latter phase will be treated in a future paper.