

Edgar F. Westrum, Jr., for the many helpful discussions of, and encouragement for the research. Ralph M. Olson and other members of the Electromagnetic Material Reserach Laboratory aided greatly in equipment and material fabrication and procedural techniques.

APPENDIX

The development for the cubic system can be found in Gan's⁶ paper. The limitations to strong and weak fields are carried over.

Because the behavior of magnetite in the order-disorder temperature range was of prime interest, it was desired to evaluate both of Gan's Eqs. (35) and (37) just above the ordering temperature. The best available values for anisotropy constants in this region are those of Bickford.¹⁴ The equations and values are listed below and give the magnetization equations for polycrystalline magnetite in either weak or strong fields

¹⁴L. R. Bickford, Jr., J. M. Brownlow, and R. F. Penoyer, Proc. Inst. Elec. Engrs. (London) **104**, 238 (1956).

at -153°C .

$$\begin{aligned} K_1 &= 42 \times 10^2 \text{ J/m}^3, \\ K_2 &= 20 \times 10^2 \text{ J/m}^3, \\ J_s &= 498 \times 10^3 \text{ A/m}. \end{aligned}$$

Weak fields:

$$\bar{\Omega} = 0.8312 + 0.1496\zeta - 0.08705\zeta^2 + \dots, \quad [\text{Gan's (35)}]$$

where

$$\begin{aligned} \zeta &= \mu_0 J_s H / K_1, \\ \bar{\Omega} &= \bar{J} / J_s = (0.8312 + 22.3 \times 10^{-6} H \\ &\quad - 5.70 \times 10^{-10} H^2 + \dots). \end{aligned} \quad (\text{A1})$$

Strong fields:

$$\begin{aligned} \bar{\Omega} &= 1 - \left[\frac{8}{105} + \frac{16}{1155} \frac{K_2}{K_1} + \frac{8}{5005} \left(\frac{K_2}{K_1} \right)^2 \right] \frac{1}{\zeta^2} \\ &\quad - 0.05201 \frac{1}{\zeta^3} + \dots, \quad [\text{Gan's (37)}] \end{aligned}$$

$$\bar{\Omega} = \frac{\bar{J}}{J_s} = \left(1 - \frac{6.42 \times 10^6}{H^2} - \frac{1.57 \times 10^7}{H^3} + \dots \right). \quad (\text{A2})$$

Heat Capacity of Palladium and Dilute Palladium: Iron Alloys from 1.4 to 100°K

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Heat-capacity measurements have been made on pure palladium and a series of dilute palladium-iron alloys over the temperature range 1.4 to 100°K. All alloys exhibit a ferromagnetic specific heat anomaly, the entropy of which is proportional to iron concentration. This entropy corresponds to a mean spin of 1.1 ± 0.3 per iron atom. The disagreement between the latter figure and the value obtained from the saturation moment of more concentrated alloys is discussed. For the most concentrated alloy a $T^{3/2}$ spin-wave term is observed, the magnitude of which is in approximate agreement with theory. The Debye θ for pure palladium appears to have an anomalous temperature dependence.

I. INTRODUCTION

THE saturation moment of dilute palladium-iron alloys was first measured by Crangle,¹ who found ferromagnetic behavior in all cases, with an abnormally large mean moment per iron atom. This result was interpreted as being due to the polarization of those palladium atoms adjacent to each solute atom. If it is assumed that the exchange interaction polarizes each of these palladium atoms to the extent of 0.6 holes, the number presumed to exist in the $4d$ band of pure palladium, it may be shown that approximate agree-

ment with experiment is obtained. As shown by Clogston *et al.*,² however, such an assumption cannot easily be reconciled with the observed moments on Pd-Rh dilute iron alloys. Instead, they propose a model, based on the work of Anderson³ and Wolf,⁴ which gives a total spin depending on the *density of states* at the Fermi level, rather than the number of unfilled states in the d band. Such a model satisfactorily explains the observed correlation of local moment with susceptibility.

The existence of an abnormal spin moment, associated with these alloys on either model, should be readily observable in terms of the spin-dependent entropy of

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¹J. Crangle, Phil. Mag. **5**, 335 (1960).

²A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).

³P. W. Anderson, Phys. Rev. **124**, 41 (1961).

⁴P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

such systems. Since the Curie point of very dilute alloys lies either in or slightly above liquid helium temperatures, where the lattice entropy is quite small, the spin entropy of such systems should be readily measurable. For this reason, heat-capacity data in the region 1.4°K up to 100°K have been obtained for a series of very dilute palladium-iron alloys, the maximum iron concentration being about 1.7 at.%. The results indicate that the initial slope of spin entropy, as a function of iron concentration, corresponds to a total spin of 1.1 ± 0.3 . This value differs considerably from the value obtained from saturation moment data on more concentrated alloys; possible reasons for this discrepancy are discussed. For the most concentrated alloy a $T^{3/2}$ spin-wave term is observed, the magnitude of which is consistent with the polarization of those palladium atoms adjacent to each iron atom.

II. EXPERIMENTAL PROCEDURE

Heat-capacity measurements were made using a standard calorimeter described previously.⁵ To simplify the experimental procedure, an encapsulated arsenic-doped germanium thermometer⁶ was employed. In the liquid helium range, this thermometer was calibrated against vapor pressure in the usual manner. It was found that the resistance, as a function of temperature, followed quite closely the empirical relation

$$\ln T_R = a(\ln R)^2 + b(\ln R) + c, \quad (1)$$

a , b , and c being appropriately chosen constants.⁷ The deviation $\Delta = T - T_R$, in terms of the resistance R , was reproducible to better than one millidegree, thus eliminating the need for subsequent calibration. To avoid the possibility of inadvertent damage to the thermometer and heater assembly, it was fitted into a copper-beryllium collar, which was clamped to the specimen being measured. The heat capacity of this entire assembly was measured in a separate experiment.

Above 4.2°K heat-capacity data were measured in the same calorimeter, which was again used isothermally. It was possible to obtain satisfactory data up to 100°K with the can immersed in liquid helium. The germanium thermometer was calibrated in this temperature range against a Honeywell standard thermometer (Model No. 808-176P-IIC). It was here found convenient to employ an empirical relation

$$\ln T_R = a \ln R + b \quad (2)$$

and to express the calibration data in the form of the deviation $\Delta = T - T_R$ as a function of the resistance R . To cover the entire range of temperature, a number of different values of the constants a , b were employed.

⁵ J. A. Rayne, Phys. Rev. **108**, 22 (1957).

⁶ Minneapolis-Honeywell, Model No. 808-248-II.

⁷ The constants a , b , and c are substantially constant for all Honeywell thermometers of this type. This point, together with a detailed analysis of the reproducibility of such thermometers, will be discussed in a future paper.

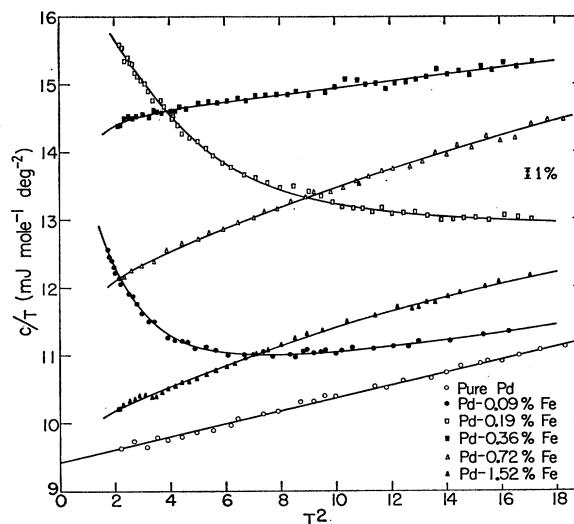


FIG. 1. Plot of C/T versus T^2 below 4.2°K for dilute palladium-iron alloys.

Sufficient overlap was allowed between successive temperature intervals, to ensure that the heat-capacity data joined together in a smooth fashion.

The specimens used in this work were induction melted under argon from 99.99% pure palladium sponge and a master alloy containing 2.65 wt.% iron, as determined by chemical analysis. Stabilized zirconia crucibles were used for containing the melt, which was stirred with a quartz rod to ensure adequate mixing. Subsequent chemical analysis showed little inhomogeneity in the resulting ingots. The composition of the specimens was, in all cases, determined by direct computation from the relevant proportions of palladium and master alloy in the melt. The specimen of pure palladium was identical to that employed by Hoare⁸ in his measurements on the silver-palladium system.

III. RESULTS AND DISCUSSION

(a) Magnetic Heat Capacity

The specific-heat data below 4.2°K are shown in Fig. 1 as the usual plot of C/T versus T^2 . For pure palladium, there is a good fit to a linear relation

$$C/T = \gamma + \beta T^2, \quad (3)$$

with $\gamma = 9.42 \pm 0.02$ mJ mole⁻¹ deg⁻² and Debye temperature $\theta = 273.6 \pm 1.4$ °K [$\beta = (12/5)\pi^4 R/\theta^3$]. These values are in good agreement with those obtained by Hoare, the Debye temperature agreeing well with that calculated from the low-temperature elastic constants of palladium.⁹ Figure 2 shows the specific heat of palladium over the temperature range 1.4 to 100°K, together with the earlier data of Clusius,¹⁰ extending down

⁸ F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) **A240**, 42 (1957).

⁹ J. A. Rayne, Phys. Rev. **118**, 1545 (1960).

¹⁰ K. Clusius and L. Schachinger, Z. Naturforsch. **2a**, 90 (1947).

TABLE I. Heat capacity data for palladium between 4 and 100°K.

Temp (°K)	C_p ($J \text{ mole}^{-1} \text{ deg}^{-1}$)	Temp (°K)	C_p ($J \text{ mole}^{-1} \text{ deg}^{-1}$)
4.42	0.047	24.38	1.66
5.15	0.062	26.33	2.06
6.24	0.084	28.59	2.47
7.08	0.102	30.57	2.88
7.16	0.104	32.47	3.30
8.24	0.131	34.72	3.86
9.15	0.159	36.66	4.38
10.15	0.198	38.47	4.91
11.17	0.245	40.65	5.41
12.16	0.299	45.36	6.78
13.16	0.359	50.64	8.48
14.30	0.422	55.51	9.83
15.18	0.498	60.96	9.90
16.23	0.593	65.19	10.85
17.17	0.715	71.08	12.46
18.23	0.792	75.94	14.10
19.20	0.909	80.79	15.00
20.20	1.04	85.93	16.82
22.49	1.35		

to liquid hydrogen temperatures. As may be seen, the discrepancy between the measurements seldom exceeds 2%; in fact, this disagreement could be due to uncertainty in our thermometer calibration at higher temperatures.

Figure 1 clearly shows the existence of an excess specific heat due to ferromagnetism, in all the alloys measured. If it is assumed that the electronic and lattice specific heats remain unchanged upon alloying, then the magnetic specific heat is clearly

$$\Delta C = C_{\text{alloy}} - C_{\text{Pd}}. \quad (4)$$

This difference is plotted in Fig. 3 for each of the specimens used in this work. As may be seen, the shape of these curves in no case corresponds to the simple λ -type anomaly, characteristic of a simple ferromagnet.¹¹ This behavior is presumably due to the spatial variation of the internal field, caused by the disordered structure of the alloys. The resulting tail in the anomaly makes it difficult to obtain a precise identification of the Curie point for each specimen. If we adopt a rather arbitrary extrapolation procedure (see dashed lines of Fig. 3), the Curie temperature as a function of solute concentration has the form shown in Fig. 4. This graph also gives the data obtained by Crangle at somewhat higher iron concentrations. Clearly there is good accord between the two sets of experiments.

From the curves of Fig. 3, it is a simple matter to compute the corresponding entropy

$$\Delta S_{\text{mag}} = \int \frac{\Delta C}{T} dT = \int \frac{C_{\text{alloy}} - C_{\text{Pd}}}{T} dT \quad (5)$$

¹¹ It should be noted that the curve for the most dilute alloy is extrapolated over a considerable temperature range and that the experimental data do not in fact extend to the peak of ΔC . For this reason no great weight should be attached to the somewhat different shape of the specific heat anomaly for this alloy:

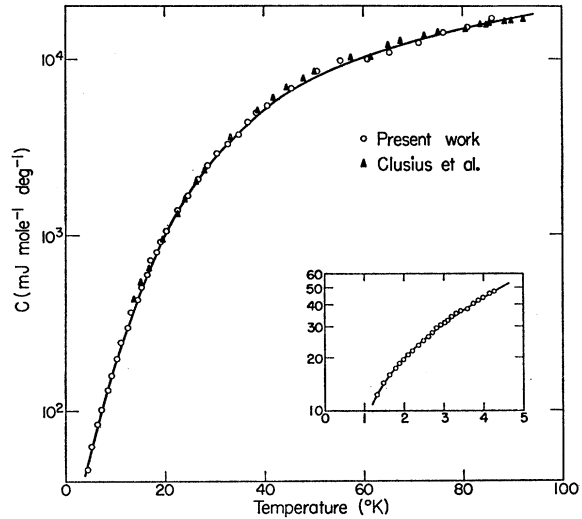


FIG. 2. Specific-heat data for palladium in the temperature range 1.4–100°K. The earlier data of Clusius are also shown.

associated with the spin ordering. This entropy is shown in Fig. 5 as a function of iron concentration; as may be seen, there is a reasonable fit to a straight line. Now from the theory of Clogston *et al.*, the total spin S_T associated with a localized spin S_0 is given by the approximate equation

$$S_T = S_0 + Z\Omega\eta(E_F)S_0J'. \quad (6)$$

Here $\Omega\eta(E_F)$ is proportional to the spin susceptibility of the solvent, Z is the number of nearest neighbors for each impurity site, and J' is an exchange integral between adjacent Wannier functions. Thus if the second term is independent of solute concentration, the magnetic entropy for a solute concentration c should be

$$\Delta S_{\text{mag}} = cR \ln(2S_T + 1), \quad (7)$$

R being the gas constant per mole; i.e., ΔS_{mag} is a linear

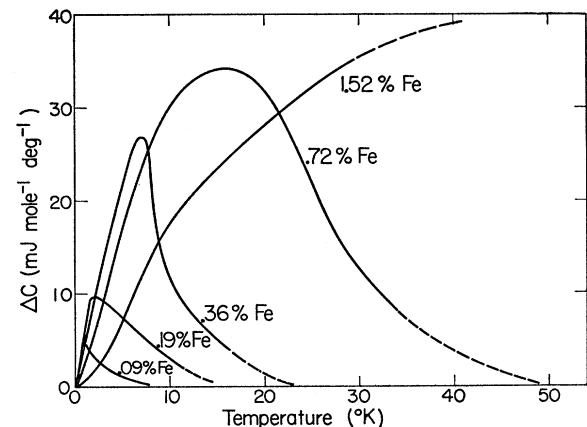


FIG. 3. Excess specific heat for dilute palladium-iron alloys. The dashed portions of the curves are extrapolated.

function of c , in agreement with experiment. From the data of Fig. 5, however, we find using Eq. (7)

$$S_T = 1.1 \pm 0.3. \quad (8)$$

This figure differs grossly from the value of $S_T = 3.7 \pm 0.4$ obtained from the magnetization data of Crangle.

A number of explanations of this discrepancy are possible. The value of S_T , corresponding to the magnetization data, is obtained assuming a g value of two. It is conceivable that this assumption is incorrect and that, for some as yet unexplained reason, a much higher g value is appropriate for iron in palladium. Another possibility is that the straight-line fit of Fig. 5 gives too much weight to the spin entropy for the most concentrated alloy. In this case, the uncertainty of the data is quite large, since the anomaly is only a small portion of the total specific heat at higher temperatures. Even disregarding this point, however, it scarcely seems possible to reconcile the discrepancy between the two values of S_T . Yet another explanation is to suppose that the

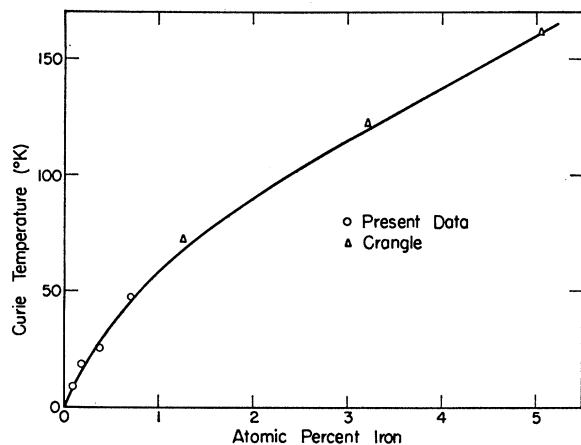


FIG. 4. Curie temperature of dilute palladium-iron alloys as a function of solute concentration. The data of Crangle are shown as triangles.

exchange interaction between solute and solvent is *not* in fact a constant and that it *decreases* for low solute concentrations. This hypothesis could, of course, be readily tested by making magnetization measurements on alloys more dilute than those measured by Crangle. At the moment, there appears to be no way of choosing between the alternatives and further experimental work on this system is needed.

As is well known, the magnetic specific heat of a ferromagnet well below the Curie temperature T_0 is given by a $T^{3/2}$ spin-wave term.¹² Thus, for $T \ll T_0$, the specific heat of the alloys studied here should be of the form

$$C = \gamma T + \beta T^3 + \delta T^{3/2}. \quad (9)$$

¹² See, for example, N. F. Mott and H. Jones, *The Theory of the Properties and Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 237.

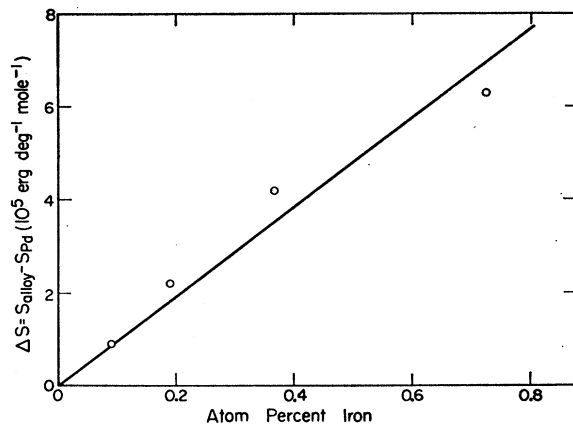


FIG. 5. Magnetic entropy for dilute palladium-iron alloys as a function of solute concentration.

Hence a plot of $(C - \beta T^3)/T$ versus $T^{1/2}$ should be a straight line, whose vertical intercept is γ and whose slope is δ . Figure 6 shows such a plot for the most concentrated alloy, assuming that the electronic and lattice specific heats are the same as those of pure palladium. The resulting coefficient of the spin-wave term is $\delta = 5.6 \times 10^4 \text{ erg mole}^{-1} \text{ deg}^{-5/2}$. Now for a fcc structure it may be shown that¹²

$$\delta = 0.452R(k/I)^{3/2}, \quad (10)$$

where I is the exchange integral. If it is assumed that $I \sim kT_0$, Eq. (10) yields for $T_0 = 75^\circ\text{K}$

$$\delta = 5.80 \times 10^4 \text{ erg mole}^{-1} \text{ deg}^{-5/2}, \quad (11)$$

which value is an order of magnitude higher than the experimental figure. The assumption $I \sim kT_0$ probably overestimates the value of the exchange integral, so that the actual theoretical value of δ is almost certainly higher than that given by Eq. (11). Thus the discrepancy with experiment is further increased. The reason for this disagreement is, however, easy to under-

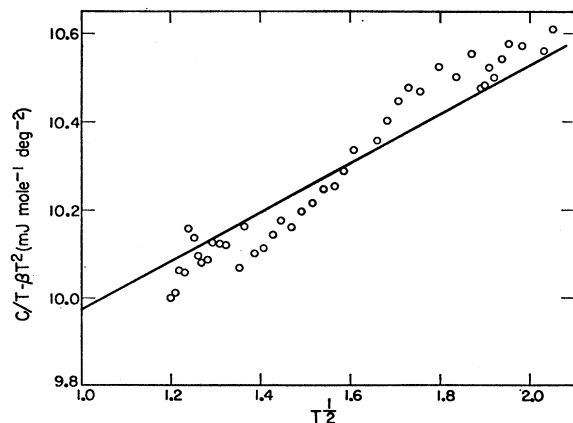


FIG. 6. Plot of $C/T - \beta T^2$ versus T for the Pd-1.52% Fe alloy. It has been assumed that the electronic and lattice heat capacity is the same as that for pure palladium.

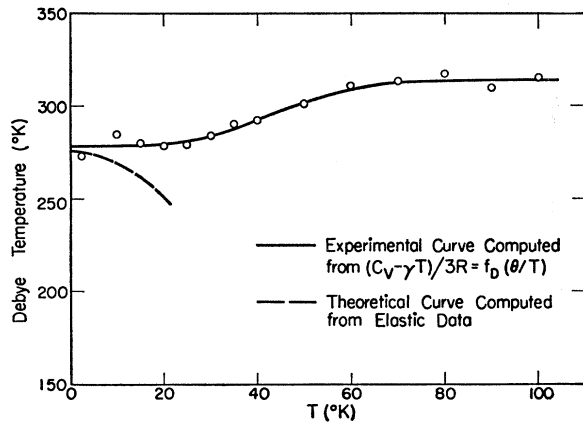


FIG. 7. Effective Debye θ for palladium as a function of temperature. The dashed line is the expected behavior calculated from elastic data.

stand. The theoretical expression (10) assumes that *all* atoms of the lattice possess a spin moment, whereas it is known that, in the present alloys, only the iron atoms and their nearest neighbors contribute to the moment. Thus, Eq. (10) should be modified to read

$$\delta = 0.452cZR(k/I)^{3/2},$$

where Z is the number of nearest neighbors for each solute atom, viz., 12 for a fcc lattice. Hence for the alloy in question

$$\delta = 1.22 \times 10^4 \text{ erg mole}^{-1} \text{ deg}^{-5/2}, \quad (12)$$

which is much closer to the experimental value.

(b) Lattice Heat Capacity

From the smoothed heat-capacity data for pure palladium, corrected from C_P to C_V and for the electronic specific heat, it is possible to compute the effective Debye θ as a function of temperature. The resulting curve is given in Fig. 7, which shows that θ increases with increasing temperature. Now if θ_0 is the value of Debye temperature computed from the elastic constants at absolute zero, it may be shown that¹³

$$\theta^3 = \theta_0^3 \{1 - f'(s, t)(T/\theta_0)^2\}, \quad (13)$$

where f' is a known function of the variables

$$s = (c_{12} - c_{44}) / (c_{12} + c_{44}) \quad \text{and} \quad t = (c_{12} - c_{44}) / c_{44}.$$

¹³ Jules de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 287.

Using the known elastic data for palladium,⁹ extrapolated to absolute zero, Eq. (13) gives

$$\theta = 275.0 - 0.06T^2, \quad (14)$$

i.e., θ decreases with temperature. It is of course possible that the model, upon which the dispersion relation (13) is based, is not correct. Nevertheless, it seems quite a general property of the vibrational spectrum in solids that the initial dispersive effects cause a lowering of the effective Debye temperature. Thus the general form of Fig. 7 is quite puzzling.

Clusius has considered the possible effects to the θ versus T curve, resulting from a deviation of the electronic heat capacity from its usual form. Since the electronic component of susceptibility χ_e is proportional to the density-of-states $N(E_F)$, it is possible to write the electronic heat capacity C_e for a free-electron assembly in the form

$$C_e = \text{const} \chi_e T, \quad (15)$$

where the constant can readily be evaluated from the values of γ and χ_e extrapolated to absolute zero. Clusius has shown that, when C_e is evaluated from (15) using the known susceptibility data, the Debye θ is substantially independent of temperature over quite a wide temperature interval. Even supposing this procedure is valid,¹⁴ however, it does not appear possible to reconcile the marked discrepancy between the two curves of Fig. 7 at low temperatures. Thus the anomalous behavior must have some other explanation.

IV. CONCLUSION

Heat-capacity data on dilute palladium-iron alloys shown the existence of an ferromagnetic anomaly, the entropy of which corresponds to a mean spin of 1.1 ± 0.3 per iron atom. The disagreement between this figure and the value obtained from the saturation moment of more concentrated alloys is not understood. A $T^{3/2}$ spin-wave specific heat is observed in the most concentrated alloy, the magnitude being in approximate agreement with theory. The Debye temperature θ for pure palladium increases with increasing temperature, in contrast to the behavior predicted from the low-temperature elastic data. No explanation of this effect has as yet been adduced.

¹⁴ The validity of (15) is open to question when applied to transition metals, owing to the effects of exchange interaction. See, for example, F. E. Hoare, J. C. Matthews, and J. C. Walling, *Proc. Roy. Soc. (London)* **A216**, 502 (1953).