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Thermoelectric Power of Palladium Based Dilute Alloys

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Abstract. The thermoelectric power, S , of palladium alloyed with 1 at.% of Ti, V, Cr, Mn, Fe, Co, Ru, Re, Os or Te has been measured between 1.5°K and 273°K. A change in the slope of $S(T)$ near the Curie temperature is observed for the ferromagnetic alloys. The PdCr alloy shows a large positive value of S at low temperature, presumably associated with an effect similar to that observed in alloys based on the noble metals (Kondo effect). For the other alloys, S is generally positive and greater than when the same dilute elements are dissolved in noble metals, but is not anomalously dependent with temperature.

Introduction

The Kondo effect is more especially observed in noble metals containing a small amount of magnetic impurities. It is experimentally characterized by a minimum of resistivity, associated with a 'giant' value of the Seebeck coefficient S . However, some alloys having a transition metal as solvant show similar effects, although some theoretical arguments predict the disparition of such a phenomena. Recent works [1, 2] have shown that PdCr alloys are an example of this kind of metal. It is consequently interesting to look at this problem more in detail from the experimental point of view, especially by using other elements than Cr as dilute metals in Pd. We report in this work measurements of the Seebeck coefficient, in a relatively large temperature range, of palladium alloyed with a series of elements of interest. The 3d transition elements are more particularly studied, the main purpose of the work being to establish if alloys other than PdCr show a similar Kondo-like behaviour.

Experimental

The alloys were melted in an arc furnace with a tungsten electrode and argon atmosphere. The purity and sources of the metals are the following: Pd (5N) Engelhard, Ti (3N) United Mineral Corporation, V (2.7N) Koch Light Laboratories, Cr (5N) U.M.C., Mn (4N) U.M.C., Fe (5N) U.M.C., Co (5N) U.M.C., Ru (5N) Engelhard, Re (4N) Engelhard, Os (5N) Engelhard, Te (5N) Fluka.

Wires of 0.2 mm diameter were drawn from the ingots for the measurements. The system used (Fig. 1) consists mainly of placing the sample between two copper blocks having different temperatures. The block A is constantly kept at the cryogenic

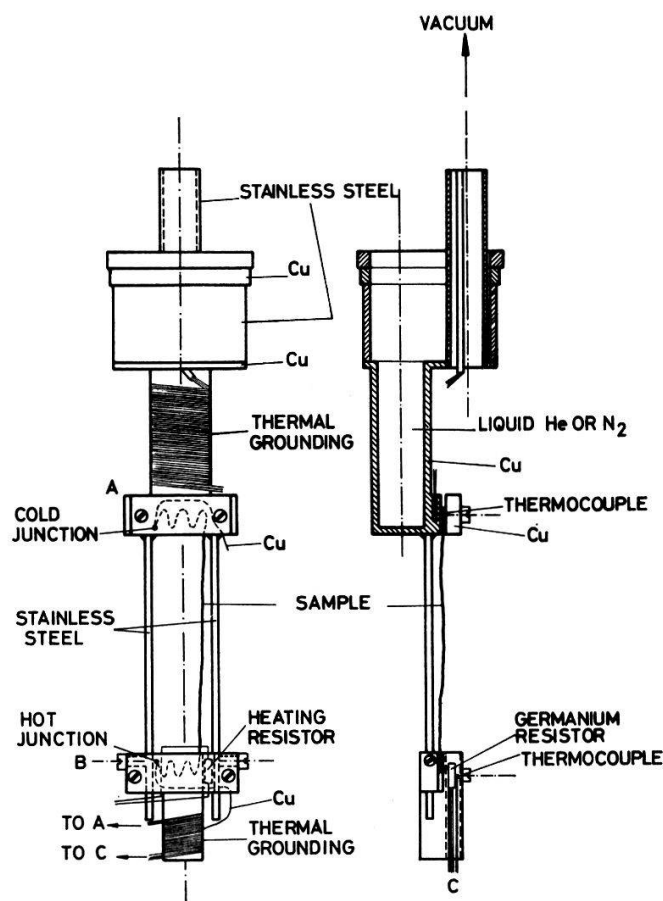


Figure 1
Apparatus for low temperature measurements of the thermoelectric power.

bath temperature (liquid nitrogen or helium). Its geometry is such that the cooling liquid stays very close to the sample extremity. The block *B* can be heated. Its temperature is measured with a calibrated germanium resistor (from Honeywell Inc.) below 40°K and above 40°K by a copper-constantan thermocouple whose two junctions are at *A* and *B* temperatures. The block *B* can be vertically displaced to accommodate samples of different lengths and it is supported by two stainless steel rods whose diameter (2 mm) is calculated so that the temperature of *B* is stable without excessive heating. Both blocks possess a cylindrical part used for thermal grounding of the wires. The germanium resistor and the thermocouple junctions are placed in small holes of slightly larger size, filled with varnish or vacuum grease to insure good thermal contact. Both ends of the sample are kept at their respective block temperatures by slightly pressing a large enough part of the wire between the corresponding block and a screwed copper piece. Electrical insulation is provided by cigarette paper and the remaining space is filled with vacuum grease to improve thermal contact. A soldered cylindrical cap allows the system to stay in 10^{-5} mmHg of pressure. A hard-soldered stainless steel piece ensures thermal insulation of the system of measure during soldering of the cover.

The thermoelectric voltage across the sample is taken by two copper wires and measured with a Honeywell 2783 potentiometer followed by a Keithley 147 nanovoltmeter. The derivative of this voltage relative to the temperature of *B*, corrected for the contribution of the copper wires, gives the absolute Seebeck coefficient of the sample. To avoid a change of the characteristics of the copper wires by too much heating, Wood's metal is used when soldering them to the sample ends.

The temperature of B is determined below 40°K by quadratic interpolation of the calibration table (the table gives values of the germanium resistance every 0.25°K below 5°K and every 2°K near 40°K). To take account of small possible changes between copper-constantan thermocouples of different sources [3], a separate thermocouple was made, and the thermoelectric voltages between 4.2°K and 77°K and between 77°K and 273°K were measured. We then corrected the table of Powell et al. [4]. Above 77°K , the sensitivity was changed by a temperature independent value. Below 77°K , the table was adjusted to make the derivative of the sensitivity continuous at 40°K . The thermocouple was calibrated below 40°K with the help of the germanium resistor. With each sample, check was made near 40°K that both systems (thermocouple and germanium resistor) indicate the same temperature.

The thermoelectric voltage of the sample is measured at temperature intervals progressively increasing as the temperature of B increases (typically, measurements were done every 1°K below 10°K and every 10°K near room temperature).

It is of course necessary to know with accuracy the Seebeck coefficient of the copper wires (commercial pure wires from Huber AG, Pfäffikon) to get the absolute value of S for the sample. A way to make this calibration is to use a sample whose thermoelectric characteristics are well known. Pure lead is a good candidate [5]. However, problems arise because of the high thermal conductivity of this material, especially at low temperature. Better results were obtained using normal silver (from Johnson-Matthey) and a comparison with the measurements of Crisp and Henry [6] on the same metal was made by checking the thermoelectric voltage of a thermocouple lead-normal silver between different temperatures (4.2°K , 77°K and 0°C).

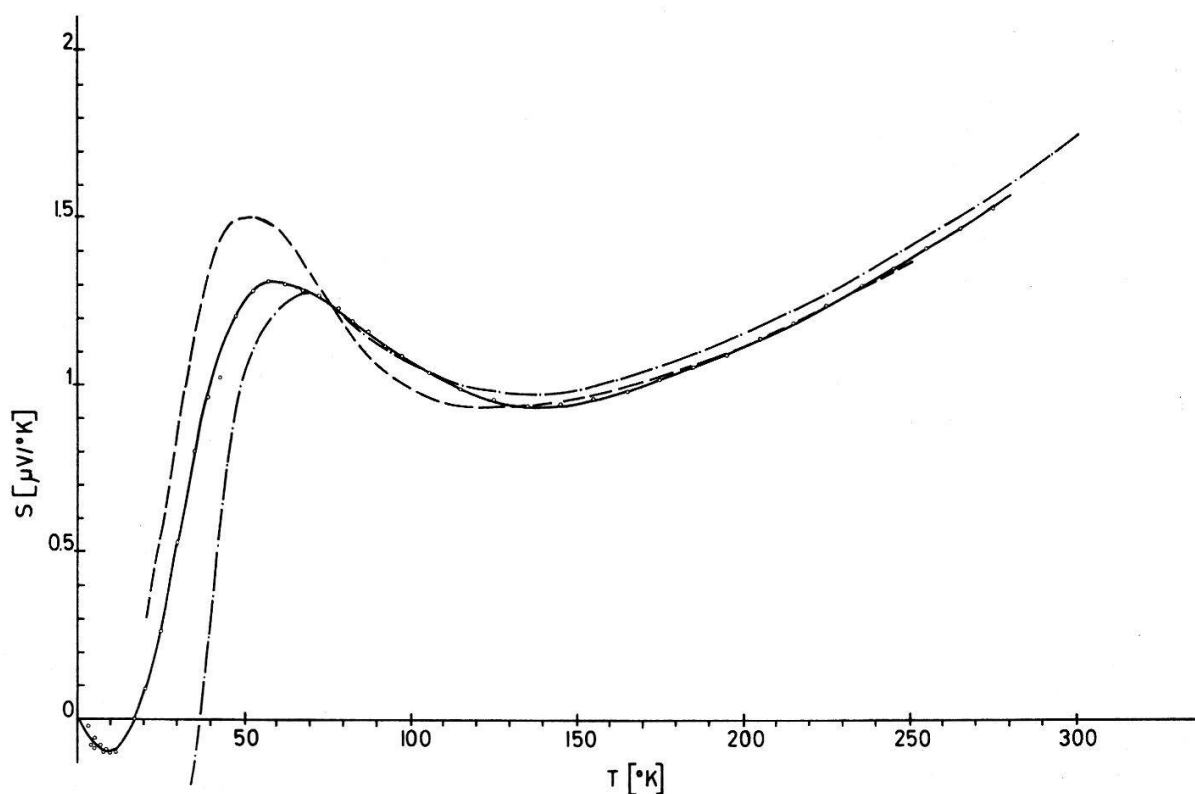


Figure 2
Seebeck coefficient of the copper wires (solid curve). Dashed curve: Ref. [7]. Mixed curve: Ref. [8].

The differences were very small. Figure 2 gives the Seebeck coefficient of our copper wires obtained when using the method explained above, together with measurements of other authors. At low temperatures, great differences between commercial coppers can exist because impurities such as iron, which produce a strong negative contribution (Kondo effect), can be present at different concentrations or partially oxydized [9]. Fortunately, our copper wire possesses only a small effect around 4.2°K , so that the correction is weak. When the absolute contribution of a sample is calculated, the accuracy is then preserved. When heating B very slowly, the absolute accuracy is of the order of $0.05 (\mu\text{V})/^{\circ}\text{K}$. Above 77°K , a good fit between data is obtained when using liquid nitrogen as cryogenic bath instead of liquid helium (the two curves $S(T)$ juxtapose within the limits of accuracy).

Results and Discussions

Pd

S for pure Pd between 1.5°K and 273°K is shown in Figure 3. It is in good agreement with the results of other authors. The positive peak having its maximum at about 60°K is attributed to phonon-drag. The slightly smaller value observed with

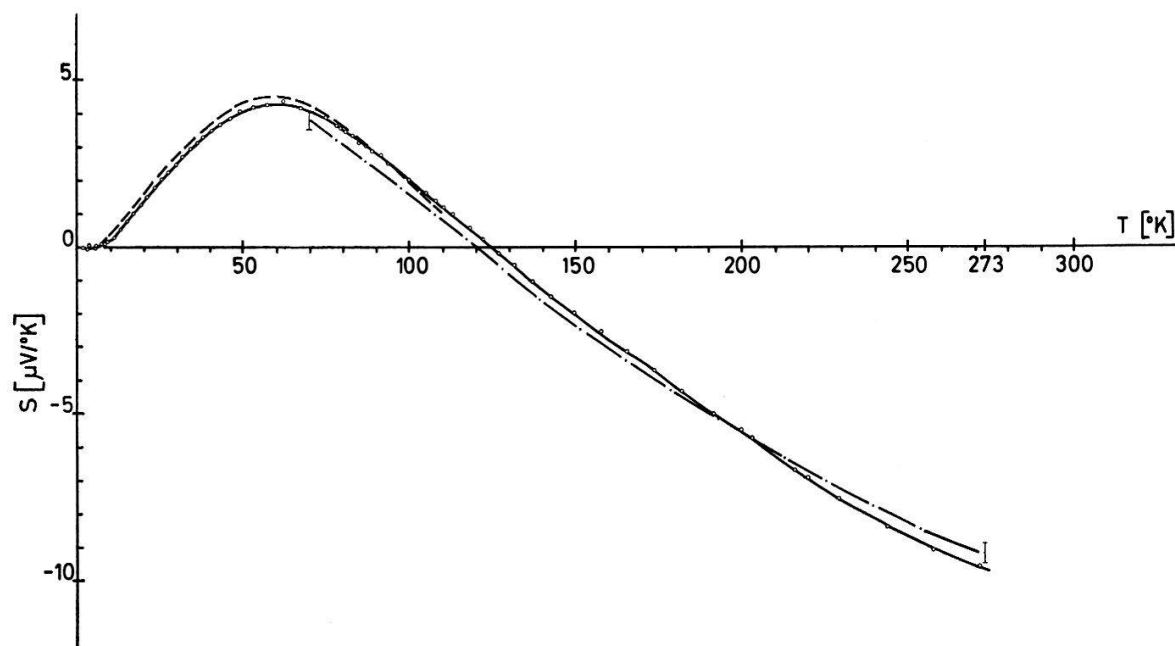


Figure 3

Thermoelectric power of Pd (solid curve). Dashed curve: Ref. [10]. Mixed curve: Ref. [11].

our sample at this temperature can be explained by the fact that it was not annealed (dislocations or impurities usually decrease the phonon-drag). At high temperature, the thermoelectric power of Pd is strongly negative. An explanation has been given by Mott [12], using a two band model. The d electrons density of states is great at the Fermi energy, and the s electrons are mainly responsible for the conductivity. Consequently, the s - d transitions are more probable than s - s transitions. As the d density of states is presumably strongly decreasing while increasing energy, we expect

the thermoelectric power to be strongly negative. Kimura and Shimizu [13] gave a more detailed calculation, using the density of states obtained from specific heat measurement in Rh-Pd-Ag.

PdCr

Only a few measurements have previously been done at low temperature on the effect of impurities on the thermoelectric power of Pd. Fletcher and Greig [14] have established a correlation between the sign of S in PdAg and PdRh alloys and the density of states given by specific heat measurements. The PdCr alloys are particularly

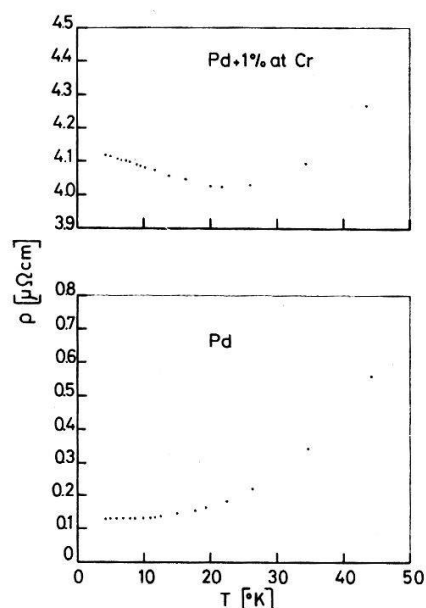


Figure 4
Low temperature resistivity of Pd and Pd + 1% at. Cr.
Samples were not annealed.

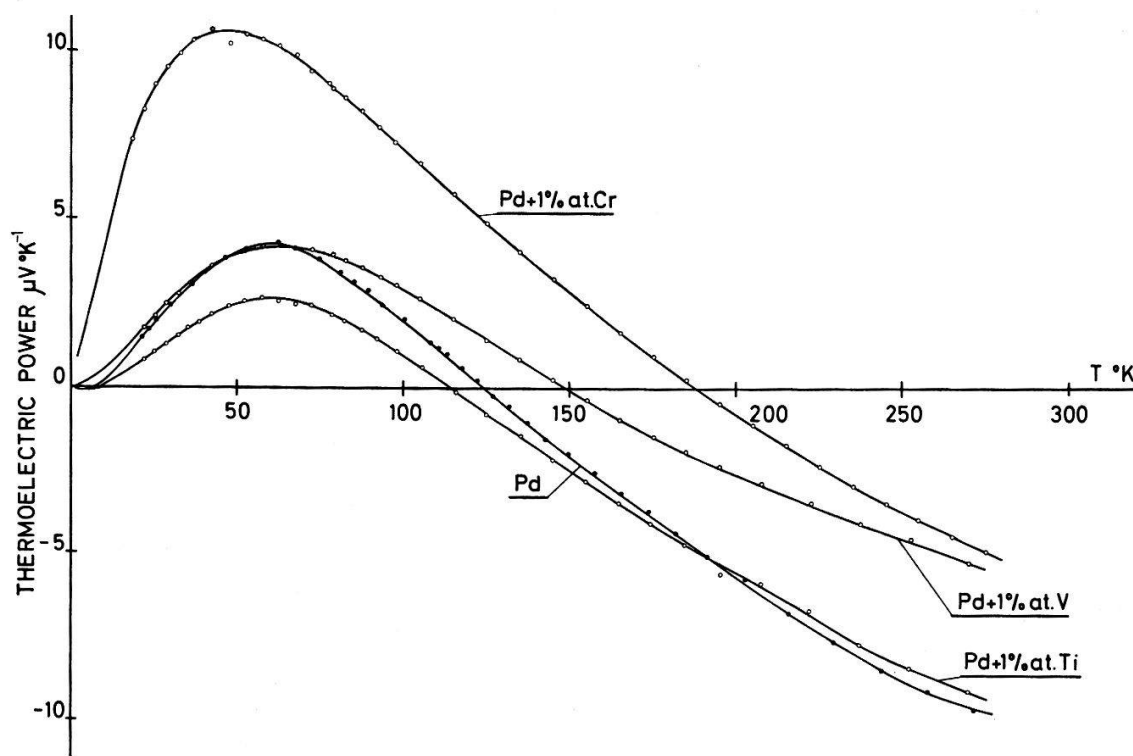


Figure 5
Thermoelectric power of PdTi, PdV and PdCr.

interesting because they give a resistivity minimum (Fig. 4), first observed by Schwaller and Wucher [1]. We have shown [2] that the same alloys present an anomalously high thermoelectric power. Figure 5 shows that at about 40°K S is of the order of + 10 (μV)/°K for an alloy Pd + 1% at. Cr, and presents some similarities with that of dilute AuV alloys [15] which give a positive peak at about 200°K. In PdCr, the temperature giving the maximum effective contribution of Cr to the Seebeck coefficient (it is not necessarily the Kondo temperature T_K [16]) is difficult to establish because the host metal already possesses high values S_{Pd} and ϱ_{Pd} . Using Nordheim-Gorter relation [7] for separating the contributions of two different scattering centers, the effective contribution of Cr is:

$$S_{Cr} = (S_{mes.} - \Delta S_{p.d.}) \left(1 + \frac{\varrho_{Pd}}{\Delta\varrho} \right) + S_{Pd} \frac{\varrho_{Pd}}{\Delta\varrho} \quad (1)$$

where $S_{mes.}$ is the measured value of the thermoelectric power of the alloy, and $\Delta\varrho = \varrho_{alloy} - \varrho_{Pd}$. $\Delta S_{p.d.}$ is the change in phonon-drag due to the impurity introduction (usually causing a decrease). Determination of S_{Cr} necessitates accurate absolute measurements of ϱ_{alloy} and ϱ_{Pd} , especially at low Cr concentration and towards the high temperatures. Furthermore $\Delta S_{p.d.}$ is not known, and can only be estimated from measurements on other Pd based alloys. Finally, the peak of S_{Cr} is not sharp but rather broad in temperature. From our data, we conclude that T_K from thermoelectric measurements has a minimum value of about 40°K, but can have several times this value.

Analytical expressions for S in presence of a Kondo effect are scarce. If we suppose that the anomaly observed with PdCr alloys is a true Kondo effect, then Figures 5 and 7 show that when $T \ll T_K$ S is proportional to the temperature, a situation that

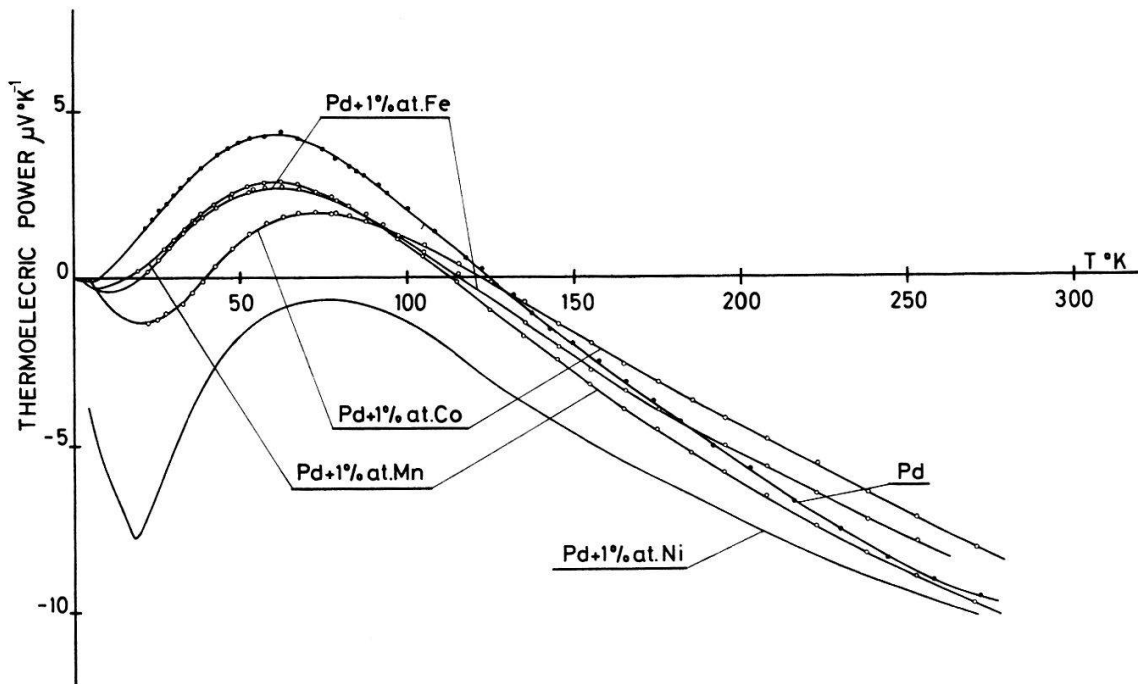


Figure 6
Thermoelectric power of PdMn, PdFe, PdCo and PdNi. The curve of PdNi is taken from Foiles and Schindler [25].

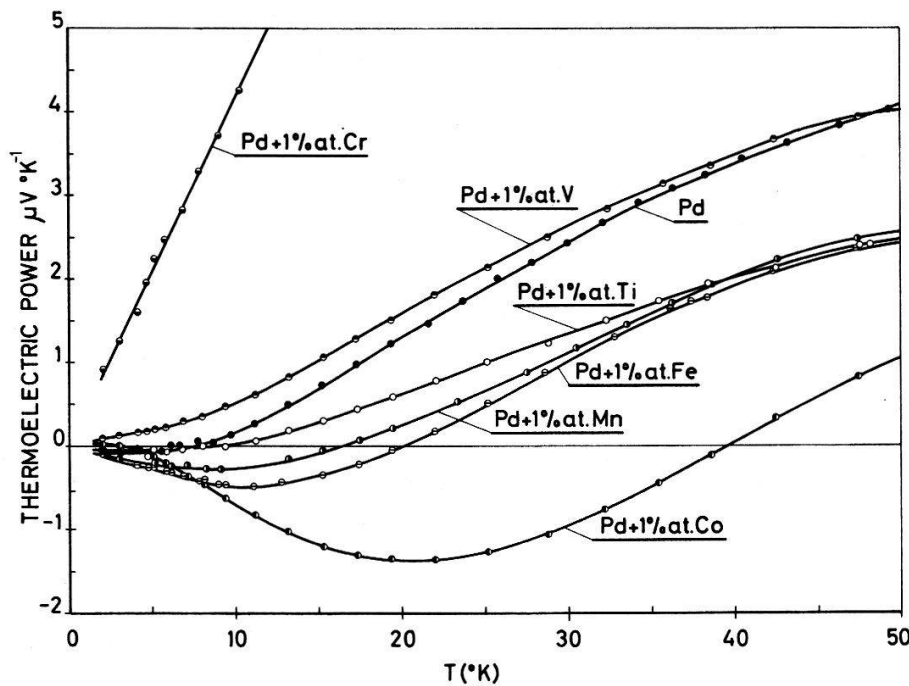


Figure 7
Thermoelectric power of
Pd + 3d elements. Detail
of the low temperature
curves.

was predicted by Rivier and Zuckermann [17]. Although their theory cannot be directly applied to the PdCr case, it is interesting to estimate T_K from their calculation: $T_K \approx k/e [1/(dS/dT)]$ and from the low temperature slope of $S(T)$ (Fig. 7) one obtains $T_K \approx 200^\circ\text{K}$.

We have previously remarked [2] that when using an alloy containing 0.5% at. Cr, S is at low temperature (when ρ_{Pd} is still small) close to that of Pd + 1% at. Cr. Hence the two alloys have almost the same S_{Cr} and separation of the curves at higher temperature is easily explained by equation (1) because $\Delta\rho$ and $\Delta S_{p.d.}$ take different values. Alloy with 0.1% at. Cr gives a somewhat lower value at low temperature. However, resistivity measurements on Pd (unannealed) indicate a resistivity relatively large at 4.2°K (Fig. 3) so that to get the effective Cr contribution in a PdCr alloy, a correction is necessary when using low Cr concentration. From the Nordheim-Gorter rule:

$$S_{Cr} = S_{mes.} \frac{\rho_{alloy}}{\rho_{alloy} - \rho_{Pd}}. \quad (2)$$

The calculated value S_{Cr} is then about the same for the three concentrations. This shows that the anomalous effect observed is essentially the fact of isolated Cr impurities and reinforce the hypothesis of a Kondo-like effect. With 4% at. Cr, however, S_{Cr} becomes much smaller, the alloy is no longer dilute, and Cr-Cr interactions begin to play an important role.

Star et al. [18, 19] have published detailed measurements of the PdCr alloys resistivity. At small Cr concentration c and at low temperature, the decrease in resistivity is proportional to cT^2 . They also observed a concentration effect: at higher concentration (4 at. %) the resistivity, instead of having a maximum as expected with RKKY interaction, is characterized by an increase of the slope $(d\rho)/cdT$. They

explained this by a coherence length effect as predicted by Nagaoka [20]. For each impurity, a certain number of electronic states is needed to form the quasi-bound state. However, if c is larger than T_K/T_F all states are used and the impurity spins are only partly compensated. From the decrease of $\Delta\rho$ towards high temperatures, they estimated $T_K \approx 100\text{--}200^\circ\text{K}$.

Several other measurements give some results similar to what is usually observed in 'Kondo alloys'. Heiniger [21] has observed an increase of the specific heat coefficient approximately linear with concentration below 1 at. % Cr. Using Nagaoka's expression $\Delta C \approx (2\pi)/3 T/T_K$, Star et al. [18] obtained $T_K \approx 200^\circ\text{K}$. Donzé [22] has measured the magnetic susceptibility of these alloys. At low Cr concentration and at low temperature, the interpretation of the results is difficult because small amounts of iron impurities give a strong increase of the susceptibility. In parallel with the concentration effect on S and ρ , a Curie-Weiss law is observed at higher concentration (2–4 at. %). An effect of magneto-resistivity was seen by Schwaller [23] only in alloys with strong Cr concentrations. Finally, we have measured at 5°K the magneto-thermoelectricity of a Pd + 0.1 at. % alloy and found a variation of S inferior to 7%, up to a magnetic field of 60 kGauss.

The different measurements in dilute PdCr suggest an effect similar to the Kondo effect as observed in noble metals based alloys. Several authors [18, 24] have noticed the analogy between the Kondo effect and the antiparallel local polarisation around Cr impurities, whereas Fe or Co impurities give a parallel polarisation in the host metal. Coupling between the Cr impurity and the neighbouring sites is progressively broken when the temperature increases, which would represent the Pd version of the Kondo effect. More theoretical work is needed to extend the Kondo theory to include the peculiarities of a host metal as Pd, particularly in taking proper account of electron-electron interactions.

PdTi, PdV, PdNi

As seen in Figures 5, 6 and 7, the other 3 d elements do not give a contribution to S as great as Cr. The only exception is Ni, measured by Foiles and Schindler [25], which produces a strong negative thermoelectric power at low temperature. The authors suggest that the origin of this phenomena is the same as for the enhancement of the T^2 term in the resistivity, i.e. spin fluctuations.

S for PdTi is small at low temperature and close to that of Pd at high temperature. Decrease in the phonon-drag peak is observed (Fletcher and Greig [10] have studied the same effect in PdAg alloys).

Vanadium gives a constantly positive contribution relative to palladium (excepted around 50°K where the decrease of the phonon-drag effect is the greatest). Daybell and Steyert [26] have reported the characteristic temperatures T_K of 3 d impurities in noble metals. T_K is minimum at the center of the series and increases very rapidly towards each end. This means that T_K of vanadium is much greater than T_K of chromium. Our results in PdV would be in agreement with a similar effect in Pd, as the small positive contribution could be the beginning of a peak at very high temperature. Figure 8 effectively shows that the relative contribution of V becomes the greatest of the 3 d series at 500°C . As will be seen later, however, even impurities

with a complete d shell can give similar results below 0°C , so that there is in fact no strong evidence for PdV alloys as having at high temperature a behaviour similar to that of PdCr alloys at lower temperature.

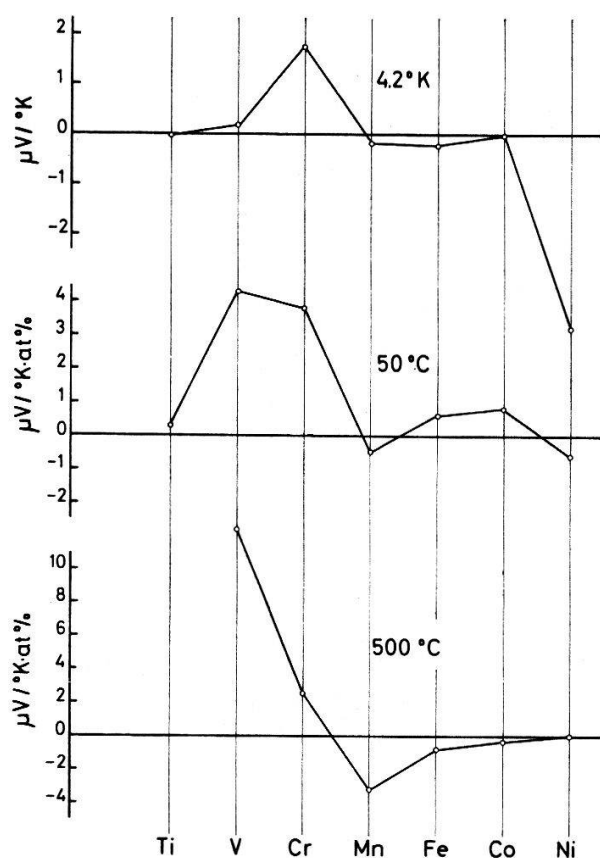


Figure 8
Effect of $3d$ elements on the thermoelectric power of palladium at several temperatures. Data at 4.2°K : our measurements, data at 50°C (more exactly: average between 0°C and 100°C): measurements of $\Delta S = S_{\text{alloy}} - S_{\text{Pd}}$ from Zwiggmann [27], data at 500°C : measurements of ΔS from Aldred [28].

PdMn, PdFe, PdCo

It is well known that these three alloys are ferromagnetic at low temperature (the Curie temperature of Pd + 1% at. Mn is about 4°K [29]). As seen on Figure 7, $S(T)$ for PdCo is not linear around 4.2°K , in contrast with the non-ferromagnetic alloys and in agreement with Kasuya's theory [30]. Schwaller [23], by resistivity measurements, has found 70°K for the Curie temperature T_C of this alloy. S presents near that temperature a tendency towards negative values relative to the PdMn and PdFe curves, manifestly connected with the onset of ferromagnetism. The same phenomena, although much weaker, appears at about 30°K for PdFe (Mydosh et al. [31] found $T_C = 29 \pm 6^\circ\text{K}$). A similar effect has been seen in nickel and is discussed by Mott [32]: spin polarization of electrons puts the Fermi energy at a value where the slope of the density of states is different. Consequently, S takes progressively a different value when crossing the Curie temperature. To observe this better in Pd alloys and to compare with resistivity measurements, we have studied an alloy Pd + 5% at. Fe, which has a Curie temperature far enough from the phonon-drag peak (Fig. 9, where T_C obtained using different techniques are plotted). Longworth and Tsuei [33] have made a detailed study of $(d\rho)/dT$ when the temperature crosses the Curie temperature. From the maximum of $(d\rho)/dT$, they find $T_C = 142 \pm 1^\circ\text{K}$. Our measurements of S , when similarly defining T_C as corresponding to the maximum

of $(dS)/dT$, give $T_C = 140 \pm 5^\circ\text{K}$. Above T_C , resistivity results show a logarithmic divergence of $(d\rho)/dT$, theoretically predicted by Fisher and Langer [35] and due to magnetization fluctuations. Although a corresponding theory does not exist for the thermoelectric power, we expect an influence of these fluctuations, as S and ρ are closely related. Effectively, $(dS)/dT$ seems linear in function of $T - T_C$ reported on a logarithmic scale (insert of Fig. 9). However, more precise measurements are needed for firm evidence, as $(dS)/dT$ is the second derivative of the measured value (the thermoelectric voltage) and consequently is relatively inaccurate.

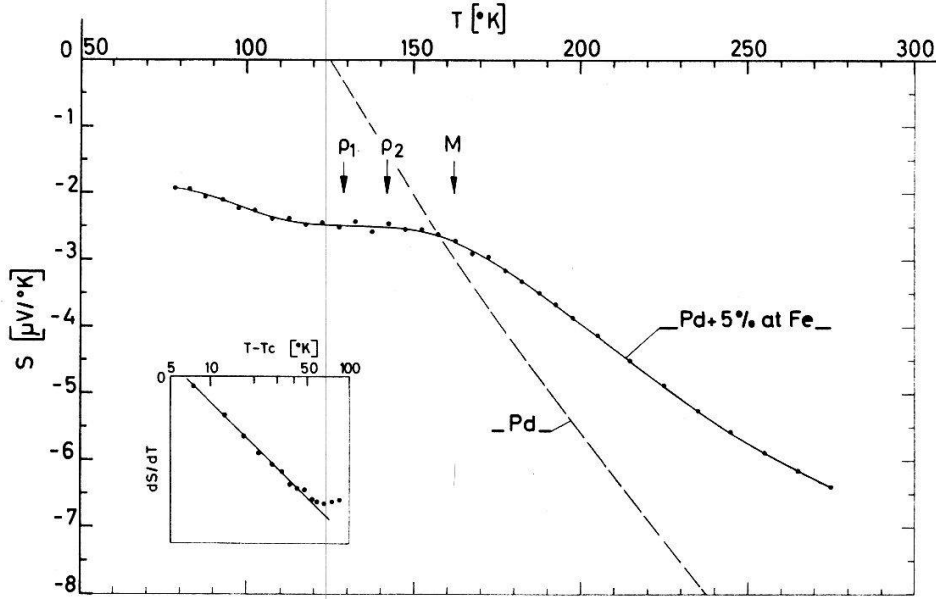
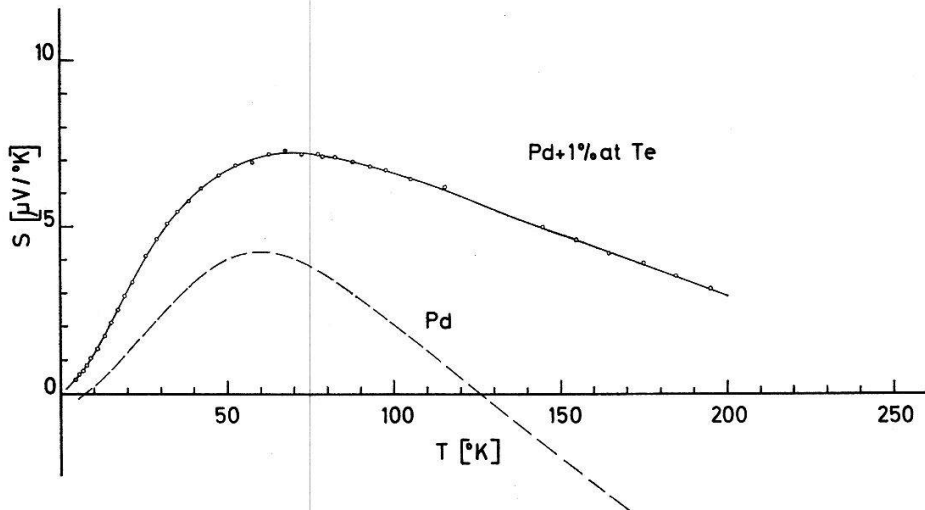


Figure 9

Thermoelectric power of Pd + 5% at Fe near the Curie temperature. The arrows represent T_C determined by different techniques. Resistivity measurements: ρ_1 and ρ_2 , respectively from Mydosh et al. [31] and Longworth and Tsuei [33]. Magnetization measurements: M , from Crangle et al. [34]. Mydosh et al. have discussed the fact that measurements other than resistivity give a value of T_C constantly greater. Insert: slope of $S(T)$ in function of $T - T_C$, with $T_C = 140^\circ\text{K}$. Dots represent values directly calculated from the $S(T)$ curve.

Figure 10
Thermoelectric
power of PdTe.

PdTe

The Seebeck coefficient for this alloy is reported in Figure 10. It can be seen that even an impurity having a complete *d* shell can give a relatively large effect. The positive value indicates that the rigid band model usually applied to Ag impurities (which give a negative effect) cannot simply be extended to impurities of higher valencies when studying transport properties, although the susceptibility simply decreases an amount proportional to the valency [36]. At room temperature, the difference $S_{\text{alloy}} - S_{\text{Pd}}$ per % impurities (after Ag) follows a simple law: $\Delta S_{\text{mes.}} = a + b(Z - 1)^3$ (whereas $\Delta \rho = a' + b'(Z - 1)^2$), where Z is the valency (Zwingmann [37]). This expression needs theoretical justification. However, this is probably the Pd version of Friedel's theory on dilute alloys [38]. The effective contribution of the impurity ΔS_{T_e} must be linear with the valency (in case of weak phase displacement) but, due to the high resistivity of Pd, ΔS_{T_e} is corrected by a contribution proportional to $\Delta \rho$ when using the Nordheim-Gorter rule to get $\Delta S_{\text{mes.}}$. The effect observed is then due to the ordinary diffusion term, with ΔS_{T_e} independent of concentration and proportional to the temperature. In a noble metal, like Ag [39], this term is usually much smaller. The low temperature slope of $S(T)$ can be calculated from room temperature measurements of ΔS_{T_e} and $\Delta \rho = \rho_{\text{alloy}} - \rho_{\text{Pd}}$ of Zwingmann, by use again of the Nordheim-Gorter rule, and can be compared with our measurements:

$$\left(\frac{dS}{dT} \right)_{\text{calc.}} = \frac{1}{323 \cdot \Delta \rho} \left[(S_{\text{Pd}} + \Delta S_{\text{mes.}}) \left(\frac{323}{293} \rho_{\text{Pd}} + \Delta \rho \right) - \frac{323}{293} \rho_{\text{Pd}} \cdot S_{\text{Pd}} \right]. \quad (3)$$

The factor 323/293 comes from the fact that the resistivity has been measured at 20°C, but S is an average between 0°C and 100°C. The value found using this formula is: $(dS/dT)_{\text{calc.}} = +0.14 (\mu\text{V})/^\circ\text{K}$, whereas from Figure 10: $(dS/dT)_{\text{mes.}} = +0.10 (\mu\text{V})/^\circ\text{K}$.

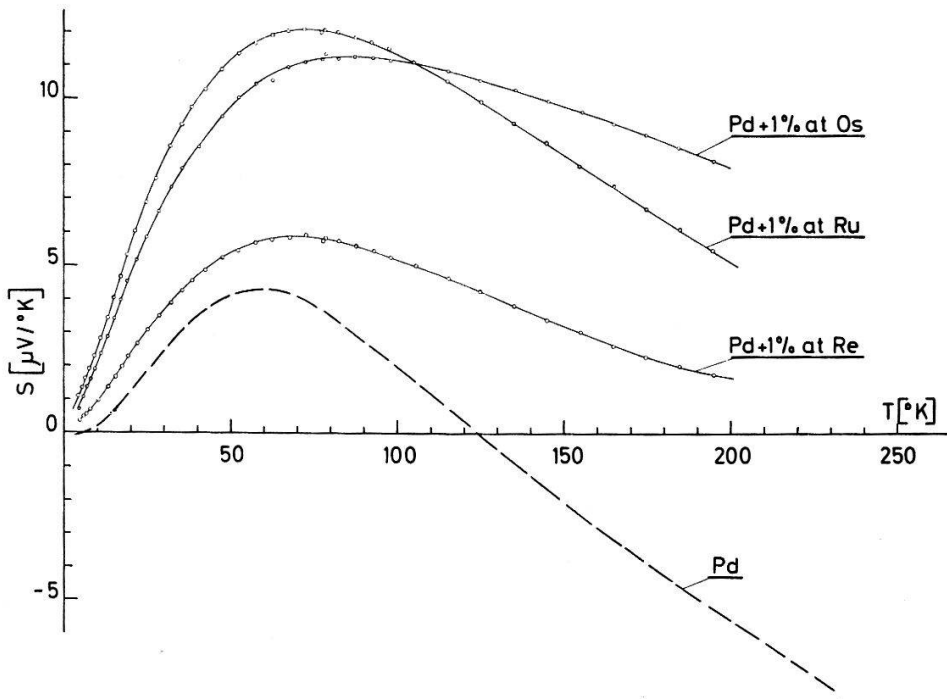


Figure 11
Thermoelectric power
of PdRu, PdRe, PdOs.

The agreement is good considering the crudeness of the calculation. For comparison, the PdCr alloys give a value of $(dS/dT)_{mes.}$ about 16.5 times greater than $(dS/dT)_{calc.}$

PdRu, PdRe, PdOs

The thermoelectric power of these alloys, between 4.2°K and 200°K, is reported on Figure 11. Relatively, great positive values are again observed, although smaller than in PdCr alloys. $\Delta S_{mes.}$ at high temperature does not follow a simple law for 4 *d* elements [37], probably because the width of the virtual state is of the same order as the band width. The shape of the density of states can then be very complicated and depends on *d* band shape and of the position of the virtual level, as calculated by Moriya [40] with Anderson and Wolff's theories. If one uses equation (3) to calculate (dS/dT) at low temperature for PdRu, the value found is again close to that measured (room temperature data are not available for PdRe and PdOs, but our measurements up to 200°K indicate a similar conclusion). This shows that the effective contribution of Ru does not vary anomalously with temperature. In parallel with this, we measured the resistivity of this alloy at low temperature to detect the eventual presence of a minimum. The variation of ρ between 1.5°K and 4.2°K is smaller than 0.001% and is consequently at least 50 times smaller than that of PdCr. Also, the introduction of Ru in Pd decreases the specific heat coefficient [41], in contrast with Cr in Pd.

Thermoelectric power at 4.2°K, measured and calculated (see text) values of dS/dT at low temperature, of palladium containing 1 at. % of dilute element.

Element diluted in Pd	$S_{4,2^\circ K}$ ($\mu V/^\circ K$)	$(dS/dT)_{mes.}$ ($\mu V/^\circ K^2$)	$(dS/dT)_{calc.}$ ($\mu V/^\circ K^2$)
Ti	− 0.04	− 0.01	− 0.024
V	+ 0.15	+ 0.036	+ 0.033
Cr	+ 1.74	+ 0.414	+ 0.025
Mn	− 0.18	− 0.042	− 0.043
Fe	− 0.22		
Co	− 0.02		
Ni	− 3.9	(− 0.93)	− 0.06
Ru	+ 1.00	+ 0.238	+ 0.150
Rh		− 0.075	+ 0.137
Ag		− 0.082	− 0.078
Te	+ 0.42	+ 0.100	+ 0.144
Re	+ 0.35	+ 0.083	
Os	+ 0.72	+ 0.171	

Conclusions

The thermoelectric power of dilute palladium based alloys has been studied with the main purpose of looking for possible Kondo-like behaviour. Comparison with noble metals based alloys has been made, more particularly on two points: 1. Magnitude of *S*. 2. Variation of *S* with temperature. *S* was found to be usually large. However, only PdCr alloys (and PdNi) give an effect varying anomalously with temperature. It is possible that some of the alloys (for instance, PdV) show an

anomalous behaviour outside of the studied temperature range. The table gives the values of (dS/dT) calculated using equation (3) assuming a 'normal' behaviour and compared with experimental values. The accord is good for the sign of S (Rh excepted) and for the magnitude of S , the two above cited alloys excepted. Ferromagnetic alloys are characterized by a change in the slope (dS/dT) near the Curie temperature. Finally, it should be noted that some of the alloys may be interesting for measurements of low temperatures, because of their great positive Seebeck coefficient (most known 'Kondo alloys' have a negative thermoelectric power at low temperature). For instance, a thermocouple Pd + 1 at. % Cr against Au + 0.03 at. % Fe has a sensitivity of about $20 (\mu V)/^{\circ}K$ between $10^{\circ}K$ and $20^{\circ}K$.

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REFERENCES

- [1] R. SCHWALLER and J. WUCHER, C.R. Acad. Sci. Paris 264, 116 (1967).
- [2] D. GAINON and J. SIERRO, Phys. Lett. 26A, 601 (1968).
- [3] R. B. SOTT, *Temperature: Its Measurement and Control in Science and Industry*, p. 206 (Reinhold Publ. Corp.).
- [4] R. L. POWELL, M. D. BUNCH and R. J. CORRUCINI, Cryogenics 1, 139 (1961).
- [5] J. W. CHRISTIAN, J. P. JAN, W. B. PEARSON and I. M. TEMPLETON, Proc. Roy. Soc. A 245, 213 (1958).
- [6] R. S. CRISP and W. G. HENRY, Cryogenics 4, 361 (1964).
- [7] D. K. C. MACDONALD, *Thermoelectricity: An Introduction to the Principles* (John Wiley & Sons 1962).
- [8] R. S. CRISP, W. G. HENRY and P. A. SCHROEDER, Phil. Mag. 10, 553 (1964).
- [9] A. V. GOLD, D. K. C. MACDONALD, W. B. PEARSON and I. M. TEMPLETON, Phil. Mag. 5, 765 (1960).
- [10] R. FLETCHER and D. GREIG, Phil. Mag. 17, 21 (1968).
- [11] J. C. TAYLOR and B. R. COLES, Phys. Rev. 102, 27 (1956).
- [12] N. F. MOTT and H. JONES, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford 1936).
- [13] H. KIMURA and M. SHIMIZU, J. Phys. Soc. Japan 19, 1632 (1964).
- [14] R. FLETCHER and D. GREIG, Phil. Mag. 17, 21 (1968).
- [15] M. D. DAYBELL, D. L. KOHLSTEDT and W. A. STEYERT, Solid State Comm. 5, 871 (1967).
- [16] M. SUHL and D. WONG, Physics 3, 17 (1967).
- [17] N. RIVIER and M. J. ZUCKERMANN, Phys. Rev. Lett. 21, 904 (1968).
- [18] W. M. STAR, B. M. BOERSTOEL, J. E. VAN DAM and C. VAN BAARLE, L.T. 11, St. Andrews (1968).
- [19] W. M. STAR and B. M. BOERSTOEL, Phys. Lett. 29A, 26 (1969).
- [20] Y. NAGAOKA, J. Phys. Chem. Solids 27, 1139 (1966).
- [21] F. HEINIGER, unpublished.
- [22] P. DONZÉ, Thesis, University of Geneva (1968).
- [23] R. SCHWALLER, Thesis, Strasbourg (1967).
- [24] I. A. CAMPBELL, Proc. Roy. Soc. (J. Phys. C.) 1/2, 687 (1968).
- [25] C. L. FOILES and A. I. SCHINDLER, Phys. Lett. 26A, 154 (1968).
- [26] M. D. DAYBELL and W. A. STEYERT, Rev. Mod. Phys. 40, 380 (1968).
- [27] G. ZWINGMANN, Metall 21, 724 (1967).
- [28] A. T. ALDRED, J. Phys. Soc. Japan 22, 762 (1962).
- [29] M. P. SARACHIK and D. SHALTIEL, J. appl. Phys. 38, 1155 (1967).
- [30] T. KASUYA, Progr. of Th. Phys. 22, 227 (1959).

- [31] J. A. MYDOSH, J. I. BUDNICK, M. P. KAWATRA and S. SKALSKI, Phys. Rev. Lett. 27, 1346 (1968).
- [32] N. F. MOTT, Proc. Roy. Soc. A156, 368 (1936).
- [33] G. LONGWORTH and C. C. TSUEI, Phys. Lett. 27A, 258 (1968).
- [34] J. CRANGLE and W. R. SCOTT, J. appl. Phys. 36, 921 (1965).
- [35] M. E. FISHER and J. S. LANGER, Phys. Rev. Lett. 20, 665 (1968).
- [36] I. R. HARRIS and M. CORDEY-HAYES, J. Less-Common Metals 16, 223 (1968).
- [37] G. ZWINGMANN, Z. Metallkunde 54, 286 (1963).
- [38] J. FRIEDEL, Suppl. Nuovo Cim. VII, 287 (1958).
- [39] B. COGBLIN, J. DELAPLACE, V. LEVY, A. A. GOMES and J. HILLAIRET, J. Phys. 29, 1096 (1968).
- [40] T. MORIYA, *Localized Magnetic Moments in Transition Metals and Alloys*, Proc. 'Enrico Fermi', course XXXVII (Academic Press 1967).
- [41] F. GAUTIER, Z. angew. Phys. 24, 289 (1968).