DEVIATIONS FROM MATTHIESSEN'S RULE FOR PLATINUM*

By P. G. Klemens† and G. C. Lowenthal‡

Summary

An analysis of the resistivity-temperature relationship down to liquid helium temperatures of 17 platinum resistors as determined in various laboratories shows that deviations from Matthiessen's rule can be classed roughly into three groups. One of them follows the pattern predicted by Sondheimer and Wilson's theory. The other two cannot be fully explained in this way, and may be due to the sensitivity of the electronic band structure of transition metals to small concentrations of impurities. The behaviour of a resistor thus depends on the nature as well as the total amount of impurities and imperfections. In low temperature platinum resistance thermometry the resistors should be selected with regard to the type of residual impurity as well as total impurity content.

I. Introduction

The electrical resistivity of metals arises from disturbances of the regular periodicity of the crystal lattice by thermal vibrations and static imperfections (impurities and physical defects). The thermal vibrations cause the " ideal " resistivity ρ_i if the lattice is otherwise perfect, the imperfections cause the " residual " resistivity $\rho(0)$ at $T=0$. Matthiessen's rule states that the electrical resistivity at any temperature T is given by

$$\rho(T) = \rho(0) + \rho_i(T), \tag{1}$$

where $\rho_i(T) \to 0$ as $T \to 0$ and $\rho(0)$ is independent of T.

Matthiessen's rule, if strictly valid, would greatly facilitate resistance thermometry, for given the resistance-temperature curve of one resistor, that of another resistor could be deduced by calibration at two temperatures only. A number of calibration procedures were suggested which are essentially based on Matthiessen's rule, and these proved reasonably reliable down to liquid air temperatures, but failed at lower temperatures. For a review of platinum resistance thermometry at low temperatures see Barber (1960).

It has become clear (e.g. Grüneisen 1933) that the resistivity shows deviations from equation (1) such that

$$\rho(T) = \rho_i(T) + \rho(0) + \Delta(T), \tag{2}$$

where $\Delta(T)$ is a function of T and $\rho(0)$, but also depends on the nature of the imperfections causing $\rho(0)$ (Mott and Jones 1936, p. 289).

Matthiessen's rule is based on the proportionality of electrical resistance to the scattering probability of the conduction electrons, and positive deviations $\Delta(T)$ occur whenever two or more groups of electrons contribute to the conductivity, provided they are affected differently by the two scattering mechanisms. Specific theories of the deviation were advanced by Sondheimer and Wilson (1947), and by Sondheimer (1950). Sondheimer and Wilson's treatment is based on a two-band model, both bands contributing to the conductivity. For such a model $\Delta(T)$ must be positive for all values of T. The term $\Delta(T)$ can be approximated by

$$\Delta T = \rho_i \cdot \rho(0)/[a\rho_i + b\rho(0)], \tag{3}$$

where a, b are positive quantities of order unity (Wilson 1953, p. 312). It follows from (3) that $\Delta(T) \to 0$ as $\rho_i \to 0$ and, therefore, as $T \to 0$, and also as $\rho(0) \to 0$. At higher temperatures (above about 30 °K) where $\rho_i \gg \rho(0)$, $\Delta(T)$ approaches the constant value of $\rho(0)/a$ and (1) appears to be satisfied, so explaining the fair degree of success achieved with the use of Matthiessen's rule in resistance thermometry above about 60 °K.
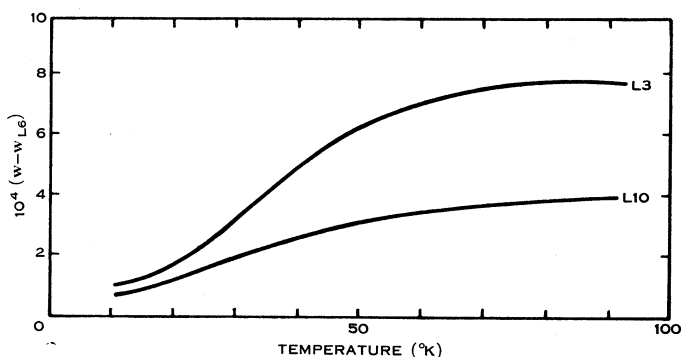

Fig. 1.—Difference in $w(T)$ between L6 and two other resistors according to Hoge and Brickwedde (1939).

The relative simplicity of (3) encouraged further attempts to use regularities in the deviations from Matthiessen's rule for the purposes of low temperature precision resistance thermometry. Van Dijk (1952, 1958) derived a number of expressions for the calculations of temperature from platinum resistance which were based partly on the results of Van der Leeden (1941) and Los and Morrison (1951) (see also White and Woods 1957) and implicitly on an expected regularity of the relation of $\Delta(T)$ with certain measurable characteristics of resistors such as their $\rho(0)$ values (obtainable by extrapolation from measurements at liquid helium temperatures) and also their α values, where α is defined by $(R_{373} - R_{273})/100R_{273}$, R being the resistance. This coefficient is the greater the purer the platinum and has long been accepted as a measure of the purity of platinum resistors ; for, although $\rho(0)$ is a more direct measure of purity than α, the former is measurable only in laboratories equipped for low temperature work.

σ

Hoge and Brickwedde (1939) reported accurate measurements of the resistance-temperature relationship of six pure platinum resistors. Some of their results are given in Figure 1. The relative resistance $w(T)$ is defined as $R(T)/R(273)$, their purest resistor was L6, so that if it is assumed that $\Delta_{L6}(T)$ is very small then $w - w_{L6}$ is a measure of the deviation of the other five resistors from Matthiessen's rule. It was pointed out by Schultz (1957) that this behaviour is in conformity with Sondheimer and Wilson's expression (3) for $\Delta(T)$.

The apparent regularity of $\Delta(T)$ found by Van Dijk and Schultz is, however, not a general property of pure platinum resistors, but a consequence of the fact that in each case attention was focused on a group of resistors from the same source, and thus having impurities of similar nature. More recent measurements on a wider group of resistors, many of even greater purity, fail to yield similar regularities, and it is clear that the deviations from Matthiessen's rule depend not only on the residual resistivity but also on the nature of the principal impurities. This will now be discussed in detail.

II. Observed Deviations

Equation (2) cannot be tested directly in the absence of an accepted procedure for the determination of ρ_i. In addition, the geometrical factor relating resistivity and measured resistance is different for each resistor and somewhat uncertain. The last-named difficulty can be overcome by using the relative resistances $w(T)$. Thus using (2) and forming the difference between two resistors having relative resistances $w(T)$ and $w'(T)$,

$$w(T) - w'(T) = \frac{\rho_i(T) + \rho(0) + \Delta(T)}{\rho_i(273) + \rho(0) + \Delta(273)} - \frac{\rho_i(T) + \rho'(0) + \Delta'(T)}{\rho_i(273) + \rho'(0) + \Delta'(273)}. \tag{4}$$

Omitting terms involving the squares of very small quantities, this difference becomes

$$w(T) - w'(T) \approx \{w(0) - w'(0)\}\{1 - w_i(T)\} + z(T) - z'(T) - w_i(T)\{z(273) - z'(273)\}, \tag{5}$$

where $w_i(T) = \rho_i(T)/\rho_i(273) \approx \rho_i(T)/\rho(273)$, and

$$z(T) = \frac{\Delta(T)}{\rho_i(273)} \approx \frac{\Delta(T)}{\rho(273)}.$$

The terms in $w_i(T)$ on the right-hand side of (5) arise because of the difference between $\rho(273)$ and $\rho'(273)$. They cannot be neglected unless $w_i(T) \ll 1$, i.e. $T \leqslant 20\ °K$, or unless $w(0) \sim w'(0)$.

Equation (5) can be used to test relative deviations, though it must always be remembered that the significance of the results of such tests must depend greatly on the characteristics of the reference resistor.

The resistors here considered are listed in Table 1. It will be seen from an inspection of their $w(0)$ values that compared with more recently made resistors even the purest (L6) of those used by Hoge and Brickwedde (1939) is now relatively impure. The resistor T4 measured by Los and Morrison (1951) has one of the lowest residual resistivities, and it is reasonable to suppose that its values of $\Delta(T)$

are also lower than those of resistors of substantially higher $w(0)$.*   This suggested the use of T4 as the standard of " quasi-ideal " resistor.   Accordingly,

$$w(T)-w_{T4}(T)+w_i(T)\{w(0)-w_{T4}(0)\}$$

has been plotted in Figure 2 as a function of T for most of the resistors listed in Table 1.   The deviations of these curves from horizontal straight lines indicate the extent to which Matthiessen's rule is not obeyed, being a measure of the quantity

$$z(T)-z_{T4}(T)-w_i(T)\{z(273)-z_{T4}(273)\}. \tag{6}$$

TABLE 1

VALUES OF $w(0)$, α, AND THE SONDHEIMER-WILSON PARAMETER $1/a$ CALCULATED FROM EQUATION (7) FOR A NUMBER OF RESISTORS

Designation	Reference*	$10^4 w(0)$	$10^6 \alpha$	Sondheimer-Wilson Parameter $1/a$ as a Function of Temperature		
				50 °K	70 °K	90 °K
T4	(1)	4·1	3926	—	—	—
G3	(2)	4·2	3927	—	small	—
Ch6	(3)	4·8†	3925‡	—	small	—
RS	(2)	9·8	3924	0·1	0·1	0·1
L6	(4)	24·0†	3917‡	0·2	0·2	0·2
L10	(4)	24·8†	3914	0·3	0·4	0·4
CT15	(5)	6·0	3926	—0·4	—0·3	+0·4
CT16	(5)	6·1	3926	—0·4	—0·3	+0·5
CT18	(5)	8·5	3924	0·3	0·3	0·7
L3	(4)	25·2†	3912	0·5	0·6	0·7
G2	(2)	4·4	3925	3	4	6
718157	(2)	5·1	3925	0·5	0·9	1·7
PS	(2)	5·9	3915	5·6	7·1	8·6
A1	(2)	7·5	3923	0·9	1·0	1·2
S1	(2)	8·9	3921	1·0	1·2	1·4
S2	(2)	8·9	3921	1·1	1·4	1·5
R10	(5)	15·7	3911	1·5	1·8	2·3

* References : (1) Los and Morrison (1951) ; (2) Barber (1958) ; (3) Chambre Centrale (1954) ; (4) Hoge and Brickwedde (1939) ; (5) Lowenthal, Kemp, and Harper (1958).

† Obtained by extrapolation from 10 °K.

‡ Estimated.

The most striking feature of these curves is their variety in shape, giving a clear indication that the deviations do not arise from a single cause.   Certainly, the two-band model of Sondheimer and Wilson cannot account by itself for these variations.   More particularly, the fact that CT15 and to a lesser extent G3 have negative values for (6) suggests that factors not considered by Sondheimer

* It will be noted, though, that resistor G2 has nearly the same $\rho(0)$ value as T4 but obviously very different $\Delta(T)$ values.

and Wilson must be operative, since the two-band mechanism does not admit of negative values of $\Delta(T)$. Of course, a negative value of (6) does not necessarily imply that either $z(T)$ or $z_{T4}(T)$ are negative anywhere. Firstly, it might merely be a reflection of a peculiarity in T4 ; but this is unlikely because a curve of CT15 versus G3 would also gives negative values. Secondly, however, is the objection that (6) may become negative because the last term might become larger in magnitude than $z(T) - z_{T4}(T)$. This would be so if the ratio $z(T)/z(273)$ was smaller than $w_i(T)$ at low temperatures, but increased faster with T than $w_i(T)$ above about 70 °K, for at 273 °K both quantities are equal. It is readily shown, however, that with $\Delta(T)$ due entirely to the two-band model (equation (3)), expression (6) would never be negative.
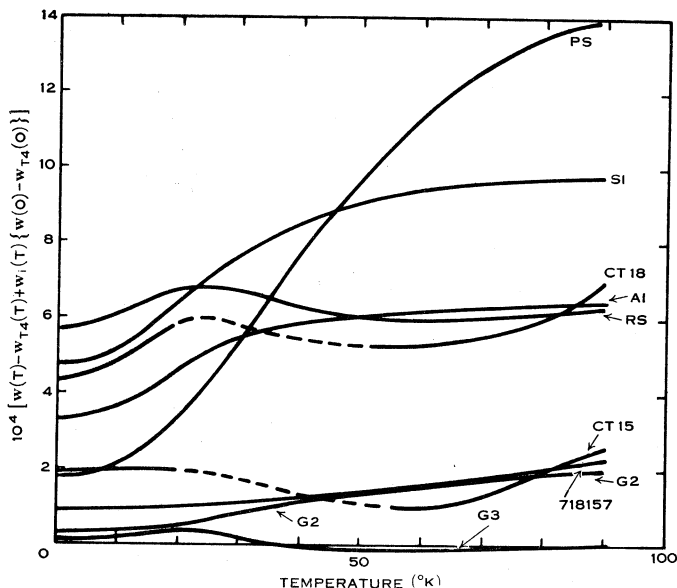

Fig. 2.—Deviations from Matthiessen's rule relative to T4 as shown by the temperature variation of $w(T) - W_{T4}(T) + w_i(T)\{w(0) - w_{T4}(0)\}$. Designation of resistors as in Table 1. Curves have been omitted for Ch6 (close to T4 and G3), CT16 (close to CT15), S2 (close to S1), and R10 (beyond range of graph).

III. CLASSIFICATION OF DEVIATIONS

To get more direct information about the extent to which the Sondheimer-Wilson theory applies to the resistors listed in Table 1, one can assume that $\Delta(T)$ is given by (3), so that for $T \gtrsim 30$ °K, where $\rho_i \gg \rho(0)$, one obtains $\Delta(T) \approx \rho(0)/a$ and therefore $z(T) = z(273) \approx w(0)/a$. Substituting this result into (5) leads to

$$w(T) - w_{T4}(T) = \{w(0) - w_{T4}(0)\}\{1 - w_i(T)\}(1 + 1/a), \qquad (7)$$

and if $\Delta(T)$ is indeed given by (3) than $1/a$ as calculated from (7) would be constant. It will be seen that this is generally not so. Instead, the resistors fall into three more or less distinct groups which are separated in Table 1 by horizontal lines. Resistors in group 1 have $1/a$ both small and constant, for

those in group 2 it is still small but increases with temperature, while those in group 3 have $1/a$ values up to ten times greater than those in group 1 and increasing rather strongly with temperature. The divisions are, of course, somewhat arbitrary, not least because the magnitudes of $1/a$ depend on the characteristics of the resistor chosen as standard. Besides, some resistors are clearly borderline cases : L3 and CT18 could have been classed into group 1 while A1 and possibly S1 and S2 could have been classed into group 2.

Clearly, the behaviour of $\Delta(T)$ or $z(T)$ depends not only on $\rho(0)$ or on α. It is seen from Table 1 that L6 and L10, which are in group 1, have a much greater residual resistivity than each member of group 3. The α values of L6 and L10, on the other hand, are higher than those of R10 and PS but lower than those of the other members of group 3. But within each group the resistors have similar deviations, and if resistors belonging to one particular group, say group 1, could be identified in a convenient way, a relatively simple formula would serve to predict their characteristics with accuracy over a wide range of temperatures. Such a formula was discussed by Schultz (1957) and an even simpler procedure was used by Lowenthal, Kemp, and Harper (1958) (see also Lowenthal and Harper 1960).

The manner in which the groups of Table 1 have been obtained here is, of course, much too cumbersome to effect identification for purposes of resistance thermometry. It is not difficult, however, to derive practical selection criteria of the type which have long been familiar in thermometry and which are now an integral part of the International Practical Temperature Scale. One such criterion has been described elsewhere (Lowenthal, Kemp, and Harper 1958).

IV. REASONS FOR DEVIATIONS

The origin of these various deviations from Matthiessen's rule is a rather complex problem and no single completely satisfactory explanation appears to exist. It is believed, though, that variations in ρ_i due to variations in electron concentration are at least partly responsible for this effect. One would expect transition metals to be particularly sensitive to small changes in electron concentrations. This would cause $\Delta(T)$ to be proportional to T at high temperatures, while the two-band mechanism and its various modifications predict that at high temperatures $\Delta(T)$ becomes constant. In terms of the relative resistivities $w(T)$, both explanations lead to qualitatively the same behaviour. To distinguish with certainty between them would require the absolute measurement of $\Delta(T)$ and, therefore, accurate measurements of the specimen geometry. This, however is very difficult to do.

V. CONCLUSION

The two-band model and its modification as proposed by Sondheimer and Wilson are not adequate by themselves to account for the three more or less distinct types of deviations from Matthiessen's rule found for " thermo-pure " platinum resistors, though it does account satisfactorily for one of these types (group 1). It would appear that the sensitivity of the electronic band structure of transition metals to small concentrations of impurities is a further mechanism producing significant deviations.

To effect precision low temperature resistance thermometry without extensive calibrations it would then be necessary to control not so much the amount of the residual resistivity but rather the nature of the impurities and imperfections which give rise to $\rho(0)$. As a probably more practicable alternative a suitable selection procedure should be used to exclude all resistors with deviations from Matthiessen's rule differing from an agreed type of deviation such as for example from group 1 of Table 1. If this is done, it is readily shown (e.g. Lowenthal, Kemp, and Harper 1958) that all resistors satisfying such a requirement have similar resistivity-temperature relationships which, therefore, are predictable over a wide range of temperatures.

VI. REFERENCES

BARBER, C. R. (1958).—*P.V. Com. Int. Poids Més.* **26** : T52.

BARBER, C. R. (1960).—Resistance thermometers for low temperatures. *In* " Progress in Cryogenics." Vol. 2. (Heywood and Co.: London.)

CHAMBRE CENTRALE DES MÉSURES ET INSTRUMENTS DE MÉSURE, URSS (1954).—Memorandum, *P.V. Com. Int. Poids Més.* **24** : T141.

GRÜNEISEN, E. (1933).—*Ann. Phys., Lpz.* (5) **16** : 530.

HOGE, J. H., and BRICKWEDDE, F. G. (1939).—*J. Res. Nat. Bur. Stand.* **22** : 351.

LOS, J. M., and MORRISON, J. A. (1951).—*Canad. J. Phys.* **29** : 152.

LOWENTHAL, G. C., and HARPER, A. F. A. (1960).—*Brit. J. Appl. Phys.* **11** : 205.

LOWENTHAL, G. C., KEMP, W. R. G., and HARPER, A. F. A. (1958).—*Bull. Int. Inst. Refrig. Annexe* **1** : 107.

MOTT, N. F., and JONES, H. (1936).—" The Theory of the Properties of Metals and Alloys." (Clarendon Press: Oxford.)

SCHULTZ, H. (1957).—*Z. angew. Phys.* **9** : 465.

SONDHEIMER, E. H. (1950).—*Proc. Roy. Soc.* A **203** : 75.

SONDHEIMER, E. H., and WILSON, A. H. (1947).—*Proc. Roy. Soc.* A **190** : 435.

VAN DER LEEDEN, P. (1941).—Doctoral Thesis, Leiden University.

VAN DIJK, H. (1952).—*P.V. Com. Int. Poids Més.* **23B** : T48.

VAN DIJK, H. (1958).—*Bull. Int. Inst. Refrig. Annexe* **1** : 101.

WHITE, G. K., and WOODS, S. B. (1957).—*Rev. Sci. Instrum.* **28** : 638.

WILSON, A. H. (1953).—" The Theory of Metals." 2nd Ed. (Cambridge Univ. Press.)