ON KLEMENS AND LOWENTHAL'S PAPER ON DEVIATIONS FROM MATTHIESSEN'S RULE*

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In a recent paper on deviations from Matthiessen's rule for platinum Klemens and Lowenthal (1961) classified the deviation patterns, calculated for a number of different platinum resistance thermometers, into three groups, and reported that only one of these groups followed the pattern predicted by Sondheimer and Wilson's (1947) two-band conduction theory. They suggested that if resistors belonging to one particular group (though no matter which group) were selected for use in low temperature platinum resistance thermometry then the resistance–temperature relationship could be expressed accurately by a relatively simple formula. We believe that Klemens and Lowenthal's method of classifying the resistors into groups is open to serious objection and that consequently some of their important conclusions are not necessarily valid.

According to Sondheimer and Wilson (1947) the resistivity $\rho(T)$ for two-band conduction can be expressed in the following manner:

$$\rho(T)=\rho_i(T)+\rho(0)+\frac{\rho_i(T)\cdot\rho(0)}{a\rho_i(T)+b\rho(0)}, \tag{1}$$

where $\rho(T)$ and $\rho(0)$ are the resistivities at temperature T °K and 0 °K respectively and the subscript i refers to ideally pure metal. The last term on the right-hand side represents the deviation from Matthiessen's rule and should always be positive. According to Wilson (1953) the quantities a and b should be of the order of unity and may be temperature-dependent.

To evaluate the parameter a (in fact they preferred to use the reciprocal) Klemens and Lowenthal used the relation given below which was derived from equation (1) for the case where $\rho_i \gg \rho(0)$

$$\frac{\omega(T)-\omega_{\mathrm{T4}}(T)}{\omega(0)-\omega_{\mathrm{T4}}(0)}=(1-\omega_i(T))(1+1/a), \tag{2}$$

and where for any given resistor $\omega(T)$ and $\omega(0)$ are the ratios of the resistivity at T °K and 0 °K respectively to the resistivity at 273 °K; the subscript T4 refers to their reference resistor T4. Their calculated values of $1/a$ for 17 platinum resistance thermometers were found to vary among the different thermometers from $-0\cdot4$ to $+8\cdot6$ and in addition were usually temperature dependent for any particular thermometer. They then classified the resistors into three groups with group 1 having $1/a$ both small and constant with temperature; group 2 having $1/a$ small and increasing with temperature; and group 3 having $1/a$ large and increasing with temperature. In conclusion, they stated that the two-

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band model of Sondheimer and Wilson does not adequately account for the three more or less distinct types of deviation from Matthiessen's rule, though it does account for the type in group 1.

Since Wilson has stated that the parameter a may be temperature dependent, we feel that groups 2 and 3 agree with the theory to about the same extent as group 1. However, a more serious objection to this work is the fact that many of the $1/a$ values are highly inaccurate because equation (2) becomes quite unreliable for resistors of purity similar to the reference resistor T4. This results from the fact that the quantities $\rho(T)$ and $\omega(T)$ may deviate from that for ideally pure platinum in a different manner for each resistor. Consequently, the quantity $(\omega(T)-\omega_{T4}(T))$ depends not only on $(\omega(0)-\omega_{T4}(0))$ but also to some extent on

TABLE 1

SONDHEIMER-WILSON PARAMETER $1/a$ AT 90 °K FOR DIFFERENT REFERENCE THERMOMETERS

Designation	$10^4\omega(0)$	$10^6\alpha$	359	T4	G2
359	3·1	3927	—	2·4	3·2
T4	4·1	3926	2·4	—	6·0
G2	4·4	3925	3·1	6·0	—
CH6	4·8	3925	0·6	—1·8	—7·7
718157	5·1	3925	2·0	1·7	—0·2
PS	5·9	3915	6·4	8·6	9·1
CT15	6·0	3926	1·1	0·4	—0·7
CT16	6·1	3926	1·1	0·5	—0·5
A1	7·5	3923	1·5	1·2	0·7
CT18	8·5	3926	1·0	0·7	0·3
S1	8·9	3921	1·1	1·4	1·1
S2	8·9	3921	1·6	1·5	1·2
RS	9·8	3924	0·4	0·1	—0·2
R10	15·7	3911	2·3	2·3	2·2
L6	24·0	3917	0·3	0·2	0·5
L10	24·8	3914	0·5	0·4	0·3
L3	25·2	3912	0·8	0·7	0·6

the properties of the reference resistor. This dependence becomes very significant when the purity of the given resistor approaches that of the reference resistor, and $(\omega(T)-\omega_{T4}(T))$ becomes very small; in fact under these conditions the above expression may yield unreasonably large or even negative values for $1/a$.

While Klemens and Lowenthal mention that their values of $1/a$ are somewhat dependent on the reference resistor they appear to have underestimated the magnitude of this dependence. To demonstrate its magnitude we have presented in Table 1 three sets of $1/a$ values (for 90 °K) corresponding to three different reference resistors (i.e. thermometers) T4, G2, and one of our own resistors 359. These thermometers are arranged roughly in order of decreasing purity (increasing $\omega(0)$); the purest is our reference thermometer 359, which has a lower $\omega(0)$ and higher α than any of their thermometers. It can be seen immediately that for the resistors of higher purity, comparable with that of the reference resistors, the value of $1/a$ varies greatly with the reference resistor chosen and includes negative and large positive values. As one would expect, the calculated value of $1/a$ for the less pure resistors is much less dependent on the choice of reference resistor.

It can be seen, therefore, that Klemens and Lowenthal's classification of resistors into three groups is to a considerable extent arbitrary, being strongly dependent for pure thermometers on the choice of reference resistor, and that consequently a number of their conclusions regarding this classification are not necessarily valid. The only values of $1/a$ reported by Klemens and Lowenthal that seriously conflict with the two-band theory are the negative values obtained with high purity resistors and these are almost certainly due to the limitation of the method of calculation. Their suggestion that thermometers be selected for low temperature thermometry according to their $1/a$ value may in fact be reasonable ; however, it is not possible to obtain this from equation (2) for very pure, i.e. the most desirable thermometers. Further work on this subject will be published shortly elsewhere, in a more comprehensive paper by one of us (R.J.B.).

References

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