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LETTERS TO THE EDITORS

COMMENTS ON THE PAPER "NEW MEASUREMENTS ON THERMAL CONDUCTIVITY REFERENCE MATERIALS"

RECENTLY Powell and Tye published an article in this journal on "New measurements on thermal conductivity reference materials" [1]. They begin the article, admirably enough, by describing the uses of thermal conductivity standards, stressing the necessity for "materials of accurately known thermal conductivities", and suggesting that the "need for the complete characterization of these materials is being appreciated". Had they stopped at this point, this then admittedly short article would meet with universal support and admiration; unfortunately, they proceed further, thereby not only showing that the need for specimen characterization is not nearly as widely appreciated as one might hope, but also presenting results which could not be more confusing had they been calculated to achieve this effect. For brevity, I will restrict my comments to two sections of their paper, the one on copper, which is of specific interest to us as we are currently submitting a paper on its transport properties to the *Canadian Journal of Physics* [2], and the one on tungsten, which contains an argument which one can only describe as remarkably odd.

1. COPPER

Powell and Tye present results for the thermal conductivity (λ) and electrical resistivity (ρ) for three different specimens of "high purity copper". The specimen characterization consists of a semi-quantitative spectrographic analysis of one of these materials; no other information is given. Neither does the paper contain any indication of the expected accuracy or precision of these results. A reference is provided for the method of measurement [3]; this, however, does not contain any mention of accuracy either. This reticence on the part of the writers makes it impossible to resolve the inconsistencies that appear in their results, which are as follows.

In the first place, the resistivities shown in their Table 1 for all the specimens are inconsistent with the claim of high purity for the specimen materials. For instance, Gerritsen [4] gives the value of 1·55 μΩ-cm for the (ideal) ice-point resistivity for pure copper, while Powell (R. L., *not* R.W.) *et al.* [5] give a (total) value of 1·545 ± 0·002 μΩ-cm. We ourselves have measured the (total) value on two sets of specimens of widely differing geometry, and obtained 1·545 ± 0·002 and 1·543 ± 0·003 μΩ-cm. Extrapolating Powell and Tye's results to 0°C (by fitting a quadratic to their values at 20, 50 and 100°C), one obtains resistivities of 1·64, 1·68 and 1·60 μΩ-cm for specimens 1–3 respectively, some 6, 9 and 4 per cent higher than the above values. If one therefore takes the "high-purity" claim at its face value, then the resistivities must be in error by some 3–5 per cent.

The second inconsistency lies in the temperature variation of the resistivities of specimens 1 and 3. These cross at 50°C, and suggest that there is an error in these values of some 3 per cent which does not originate in the geometrical parameters of the specimens.

The third inconsistency lies in the reported thermal conductivity values (λ) relative to ρ. For instance, at 50°C specimen 3 has a 2 per cent larger λ but same ρ as specimen 1, while specimen 2 has only a 1 per cent higher ρ while 4 per cent lower λ than specimen 3. There appears to be therefore a 3 per cent error in λ relative to the measured values of ρ. There being no description of the sources of these errors, one can only combine them additively to arrive at an uncertainty of some 6 per cent for the Lorenz "function", L. This error is equivalent to the *total* spread of all the previously reported values which are contained in Table 11 of [1]. It is difficult to see, therefore, what these "new results" contribute to the establishment of precise thermal conductivity values for pure copper.

As a final point in this section, I should like to take exception to the authors' statement that "the values of L tend to increase with increase in thermal conductivity and purity". This is contrary to what one would expect theoretically, both because in copper impurity scattering leads to higher values of L than thermal scattering, and because the phonon conductivity usually becomes relatively more important as the purity decreases. One would therefore expect L to decrease with increasing purity and thermal conductivity. This is, in a sense, substantiated by the observation that the higher values of L in Table 11 of [1] are associated with values of ρ higher than one would expect for pure copper (1·88 μΩ-cm at 50°C), and thus cannot represent the *correct* values for that material in *pure form.*

2. TUNGSTEN

Powell and Tye compare their results for tungsten obtained on material with a residual resistivity (r.r.) ratio

of 150, with those of ORNL, obtained on material with a r.r. ratio of about thirty. They find a thermal conductivity which, at 50°C, is some 5 per cent larger than the ORNL value, and an electrical resistivity which agrees with the latter almost within the quoted precision. Powell and Tye then explain their larger value of λ by the higher purity of their specimen, and the agreement in ρ as due to a (presumed) larger porosity of their specimen. This is nonsense! Porosity, within the conventional definition of the word, acts as a geometrical factor and, the ratios of the respective conductivities of tungsten to those of the pores being what they are, should affect λ and ρ near room temperature by factors equal to about one part in 10^4. There are therefore two distinct discrepancies between the results of [1] and the results of ORNL: the discrepancy between the r.r. ratios and ice-point resistivities, and the one between the thermal conductivities and electrical resistivities. Powell and Tye can explain, at least to their own satisfaction, one or the other of these discrepancies by arbitrarily assuming a suitable porosity, or the lack thereof, but they cannot have it both ways. In this connection I should like to mention that there exists an independent check on at least one parameter reported by ORNL; at their request we have measured the electrical resistivity of a specimen of their tungsten using a high-current square-wave comparator. Our results differed from theirs by $+0{\cdot}1$ per cent at 300°K and $-0{\cdot}3$ per cent at 1500°K, with a maximum deviation of $-0{\cdot}38$ per cent at 900°K.

In conclusion I would like to point out that near room temperature the results of [1] frequently deviated in a characteristic way from the results obtained in other laboratories, in having a thermal conductivity larger by 5 per cent or so relative to the measured electrical resistivities. It occurs here in tungsten ($\Delta\lambda = +5$ per cent, $\Delta\rho \sim 0$), it occurs in copper relative to our work (Sp. 1: $\Delta\lambda \sim 0$, $\Delta\rho = -3$ per cent; Sp. 3: $\Delta\lambda = +2$ per cent, $\Delta\rho = +3$ per cent) and has previously occurred in the values they reported for platinum [6, 7]. In my opinion this characteristic deviation, combined with the lack of meaningful specimen characterization, the lack of any estimate of experimental accuracy, and the internal inconsistencies, renders their results contained in the two sections that I have discussed of little value as far as precise determinations of conductivities of solids are concerned.

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M. J. LAUBITZ

Division of Applied Physics
National Research Council
Ottawa 7
Canada

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REJOINDER

LAUBITZ is correct in that many of the results presented by us [1] do not conform to the idealized requirements of our introductory remarks. These remarks were directed towards the future and its needs. Our paper never pretended to match up to these requirements. It was, as Laubitz is well aware, an attempt to present results of past work on which no further measurements were possible, and which, if not then presented, would probably have been lost