LETTER TO THE EDITOR

On the thermal conductivity and diffusivity of solid and liquid uranium dioxide

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Abstract. For a long time, the large discrepancy between the various measurements of the thermal conductivity, k, of liquid UO_2 has represented an insoluble difficulty. The recent experimental determination of the heat capacity of this material, at temperatures from 2500 K to above the melting point, makes it possible to evaluate the heat diffusivity, α, in this temperature range. A discussion of the dependence of α on temperature indicates that the lowest measured value of k is the right one.

About fifteen years ago, three laboratories in Europe and the USA [1–5] were independently asked, within the frame of the respective reactor safety projects, to start an experimental programme aimed at determining the thermal conductivity, k, of liquid UO_2. The final results, obtained after lengthy and difficult experimental work, were in such disagreement that the ensuing discussions and mutual criticisms prolonged the work of the specialists involved for several years, in a vain attempt at settling the controversy. The data and the basic features of the experiments are collected in figure 1 and table 1.

Details of the experimental techniques and of the applied analysis, as well as the discussion of their inherent merits and deficiencies, are reported in the above mentioned references, so that only the salient aspects of the experiments are reported here.

(i) The measurements performed by both Kim *et al* and Otter and Damien are based on standard methods (respectively, temperature-wave and temperature-flash). These methods are normally applied under conditions enabling the thermal diffusivity to be directly obtained (corrections, accounting for energy losses, are eventually applied, based on validated algorithms); however, in the cases examined, owing to the complicated specimen mountings, energy transport instead of the temperature diffusion equation had to be considered. This involved the assessment of the heat capacity of the various system components and the power balance at the boundaries. The analysis of the experiments is therefore much more complex than that used in the respective standard methods [6]. This is a crucial consideration in the evaluation of the measurement accuracy.

(ii) The experiment performed by Tasman *et al* is, at first sight, the most uncertain since it is intrinsically affected by precision limits, mainly imposed by the presence of very high radial temperature gradients as well as axial asymmetries. However, in spite of that, the error in k is bounded by the experimental localization of the melting front which
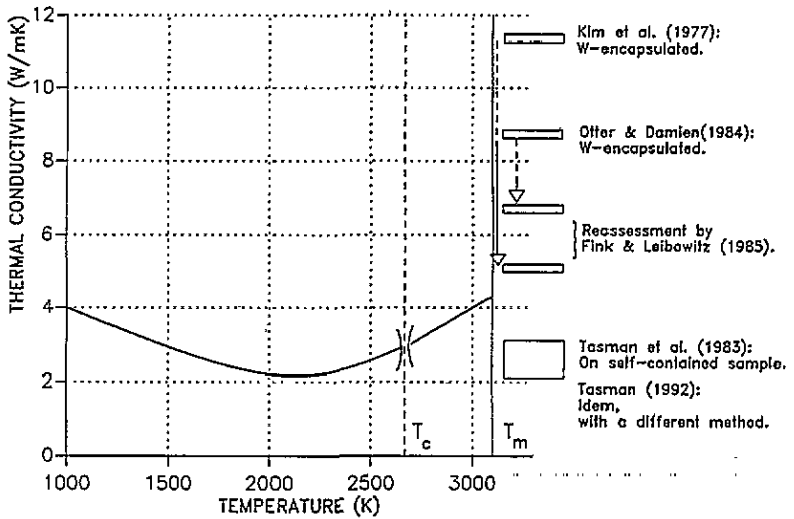
Figure 1. Measured thermal conductivity in solid and liquid UO_2. The temperature T_c corresponds to the observed λ transition. No discontinuity in k is measured across this temperature.

penetrates into the sample from the heated surface down to an easily measurable depth, whose determination is actually not so ambiguous as was stated in [4]†.

(iii) Furthermore, Fink and Leibowitz [4] realized that the initial treatment of the data in the above mentioned experiments was inadequate to obtain a correct value of k. Their subsequent re-elaboration of the primary data was based on a more comprehensive analysis supported by a computer code which analyses 3D heat transfer under transient conditions. The reassessed k values, reported in table 1, should be more reliable than the original ones; however, the importance of the eventual corrections give us an idea of the difficulty of the analytical problem, and of the accuracy limits of these measurements.

(iv) Finally, more recently, Tasman repeated his experiment with an upgraded instrument, using a rapid 2D temperature scanning device as well as more sophisticated mathematical analysis [5]. His numerical solution of the unsteady transport equation obtained with a 2D finite-element method led to a smaller correction (being within the experimental accuracy) than that predicted by Fink and Leibowitz. Furthermore, Tasman claims that all presently recognizable perturbations, which could not be accounted for in his analysis, can be qualitatively anticipated as leading to *negative* corrections of the resulting value of k. Finally, after analysing his second experiment, he essentially reiterates his previous statement that the liquid conductivity (2.5 ± 1 W cm^{-1} K^{-1}) is *lower* than that of the solid (3.5 W cm^{-1} K^{-1}).

In conclusion, though it cannot be excluded that the measurements of k_{liq} are still affected by residual analytical errors, at this stage any further reduction of the large initial scatter

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† It was in fact remarked that the (sharp) onset of large basaltic grain growth misled early experimenters, investigating the phase diagram, to interpret it as the melting interface, and, consequently, to assign to $T_m(UO_2)$ the erroneous value of 2700 K, so that a similar bias could have been present in the analysis made by Tasman *et al.* Actually, it can be demonstrated that, in the short duration of their experiment ($\simeq 10$ s), the sample grain growth at 2700 K is approximately 10 μm [7]. From the above mentioned experimental data the extrapolated grain growth at 3050 K is only five times larger. The solid grains are therefore still recognizable at temperatures near the melting front.

Table 1. Thermal conductivity of liquid urania.

	Reference	k (W m^{-1} K^{-1})	Method	Sample
[1]	Kim *et al* ANL (1977)	11.0	Periodic heat flow	Tungsten-encapsulated 0.8–1.2 mm thick sample: 'three-layers' mounting
[2]	Otter and Damien CEA-CENFAR (1982)	8.5	Flash	Tungsten-ecapsulated 0.7 mm thick sample: 'three-layers' mounting
[3]	Tasman *et al* JRC-ITU (1982)	2.5	Melting front penetration under surface laser heating	Self-crucible: partly molten sample
[4]	Fink and Leibowitz ANL (1984)	5.5 [1] 6.7 [2] 4.5 [3]	Re-evaluation of experiments of [1],[2],[3] using a 3D transient heat transfer computer code	—
[5]	Tasman JRC-ITU (1988)	2.5	Melting front penetration under surface laser heating; 2D scanning of the temperature field top and bottom; FEM analysis under non-steady conditions	Self-crucible: partly molten sample

to an acceptable magnitude, based on improved theoretical corrections alone, would not be convincing. Most probably, the conditions in the experiments were indeed substantially different and, in at least two of the three cases, not serving the stated purpose†.

In this perspective, a rightness criterion can only be provided by the consistency of the measured k_{liq} with other (independently measured) thermophysical properties. This check is possible in the context of recent measurements of the heat capacity of solid and liquid UO$_2$ [8], and of the features of a pre-melting transition observed in this material at temperatures around $0.8T_m$ [9].

The argument develops along the following line: the liquid heat diffusivity is evaluated from the conductivity and heat capacity for the only case (Tasman's experiment) where these quantities were measured independently of each other. The resulting curve of α as a function of temperature in solid and liquid exhibits a clear trend which reflects the temperature diffusion properties of a class of materials undergoing a pre-melting order–disorder transition analogous to that found in UO$_2$. Therefore, one concludes that the

† An additional objection to the experiments with encapsulated samples is that substantial dissolution or dispersion of tungsten in liquid urania could have affected its thermal conductivity. An experiment is presently in progress at ITU-Karlsruhe to investigate this point.

measurements of Tasman conform with the expected behaviour of $\alpha(T)$ in liquid urania.

We now consider the *high-temperature heat capacity of urania*. The properties of the heat capacity of UO_2 between 2000 K and the melting point have recently been measured and analysed [9, 10]. The empirical function $C_p = C_p(T)$ in the solid is characterized by (i) a pronounced increase with temperature due to creation of lattice and electronic defects, and (ii) the appearance of a λ transition at 2670 K, caused by cooperative defect formation in the oxygen sub-lattice. The experiment shows that this transition is absent from hyperstoichiometric UO_{2+x}, whilst in the hypostoichiometric oxide the transition is of the first order, that is to say, the oxygen Frankel-pair concentration increases continuously in the former case, whereas in the latter, a transition occurs at a temperature $T_t = T_t(x)$ from an 'ordered-oxygen' phase to a disordered one, with a sudden increase in defect concentration of nearly one order of magnitude [9]. Between these two behaviours, the stoichiometric oxide is found to undergo a second-order transition at $T = T_c = 2670$ K; the defect concentration $n = n(T)$ is continuous across the transition temperature, but $dn/dT|_{T_c} = \infty$. The measured heat capacity in the stoichiometric oxide is shown in figure 2 as a function of temperature in an interval around the λ transition.
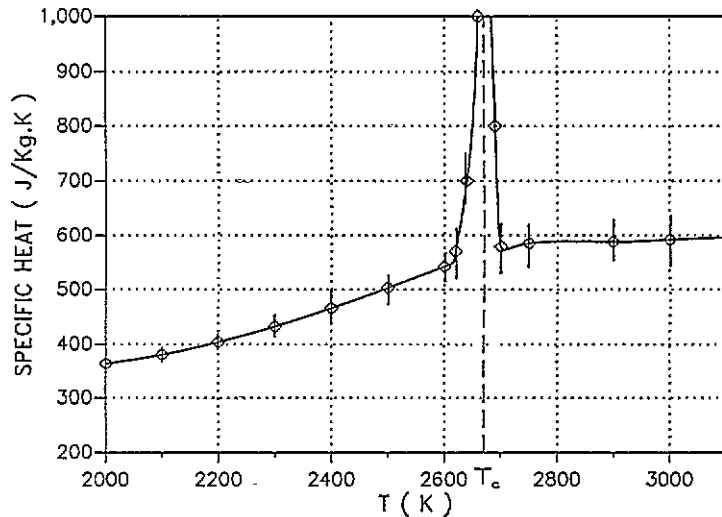

Figure 2. Heat capacity in solid UO_2 in the region of the λ transition.

The data of the liquid heat capacity, taken from [8], are shown in figure 3 from the measured solidus temperature up to 4500 K. A sharp drop in C_p is observed from the experimental point nearest to the solidus (640 J kg^{-1} K^{-1}) to that nearest to the liquidus (488 J kg^{-1} K^{-1}); at higher temperatures, the less pronounced decrease of $C_p(T)$ with T can be approximated by a parabolic dependence of C_p on $1/T$. Around 4500 K the heat capacity of UO_2 approaches the value $9R$, appropriate to the harmonic vibration in a triatomic lattice (as observed, for instance, in the case of H_2O).

Now we look at the *thermal conductivity and diffusivity*; the values of C_p plotted in figures 2 and 3 have been used to calculate the heat diffusivity, α, from the thermal conductivity. The liquid data are those measured by Tasman. Since they have been obtained, within a first approximation, in the absence of any assumption on the value of C_p in the
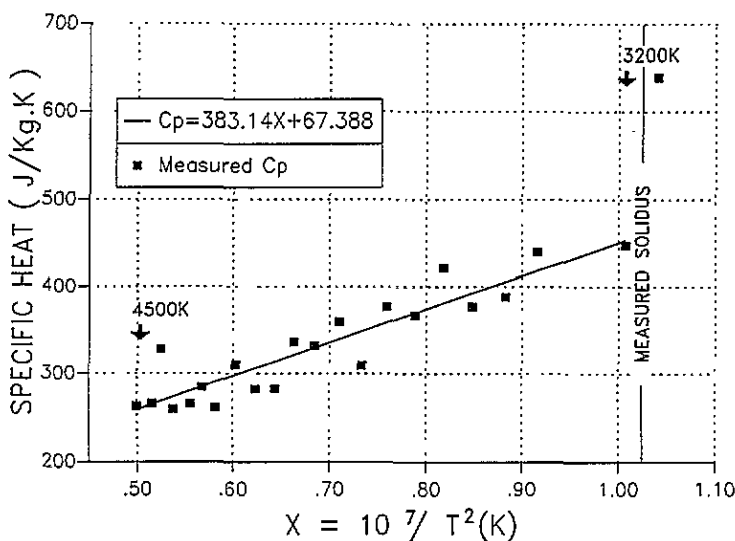
Figure 3. Heat capacity of liquid UO$_2$.

liquid†, the defining formula

$$\alpha = \frac{k}{C_p \rho} \qquad \text{(where } \rho = \text{density)} \tag{1}$$

can be used to deduce α.

Unfortunately, this procedure could not be applied to the data of [2] and [4] because k was obtained in these cases by assuming an estimate of C_p in the liquid which substantially differs from the experimental value‡.

For comparison, two sets of values of k have been adopted to calculate α in the solid: those from the MATPRO databank [11] and those used at ITU [12].

Figure 4 shows the thermal diffusivity obtained from equation (1) in the liquid and in the solid as a function of temperature. Two features immediately catch our attention.

Firstly, the diffusivity value calculated from Tasman's data is on the extrapolated line of the solid indicating no effective discontinuity across the melting temperature.

Second, the diffusivity curve in the solid is split into two segments respectively decreasing and increasing with temperature, separated by a 'pit' corresponding to the λ

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† It is worth remarking that, in the given experimental set-up, when homogeneous heating of the top surface of a disc of thickness d is produced in the absence of radial losses, the steady-state liquid penetration depth, d_{liq}, and the solid and liquid conductivities are related by the simple equation

$$k_{sol} \frac{T_m - T_{bottom}}{d - d_{liq}} = k_{liq} \frac{T_{top} - T_m}{d_{liq}}.$$

In Tasman's experiments the values of k_{liq} obtained with this simple formula are within the experimental scatter ($\pm 50\%$) of the 'correct' values.

‡ Actually, if one applies the inital one-dimensional analysis of Otter and Vandevelde [6] (which, however, was proved to be inadequate), one realizes that the correction of C_p(liq) leads to a decrease in the resulting α(liq) of approximately 50%. On the other hand, we were not able to repeat the computer code calculations of Fink and Leibowitz with the correct heat capacity assessment.
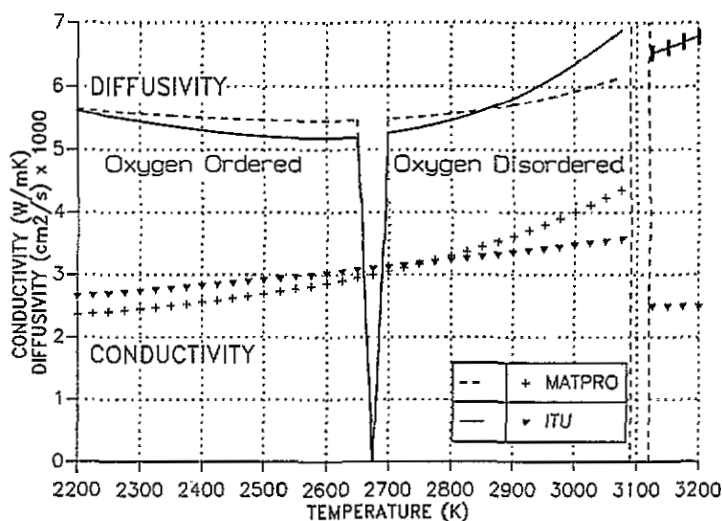
Figure 4. Thermal conductivity (recommended empirical fitting) and deduced diffusivity in UO_2. The conductivity data labelled MATPRO (crosses) are taken from [11]. Those labelled ITU (triangles) are taken from [12] for the solid, and from [5] for the liquid.

transition, which, being formally similar to a thermodynamical critical point, entails that $\alpha \to 0$ for $T \to T_c$.

Finally, *considerations of the trend of* $\alpha(T)$. The dependence of the thermal conductivity in solid UO_2 on temperature between 2000 K and T_m has been critically scrutinized (see, e.g., [12]), because the presence of a minimum in this temperature interval indicates that a distinct heat transport mechanism is activated at high temperatures. However, the complexity of the dependence of k on T makes this analysis very difficult. If the heat diffusivity $\alpha(T)$ is examined instead, a clearer insight is obtained. Diffusivity in crystals decreases with temperature due to increasing anharmonic vibrations (caused by lattice strains, impurities and defects): in this sense the regular decrease of α in UO_2 between RT and 2500 K can be qualitatively explained. By approaching the λ transition the number of phonon scattering centres dramatically increases. The zero of the dynamic quantity α at $T_c = 2670$ K is attributable to the slowness to which fluctuations decay at the critical point. Above the λ transition, in the oxygen sublattice the concentration of Frenkel pairs approaches 0.2 [10], hence the lattice displays a high degree of disorder. Making comparisons between thermal diffusivity of crystalline and glassy forms of the same substance, we realize that the dependence on temperature is opposite in the two cases, k in the glassy phase displaying an increase with rising temperature (a typical example is provided by crystalline and fused SiO_2).

Furthermore, analogous behaviour of $\alpha(T)$ is also observed in systems where electrons carry a significant part of the heat current; in fact, in a number of metals and binary alloys undergoing magnetic λ transitions around the Curie point (e.g. Fe, Ni, Co), a sharp minimum, located at the transition temperature, defines two branches of the curve $\alpha = \alpha(T)$ respectively descending (ordered) and ascending (disordered phase) with increasing T. On the other hand, in systems which do not exhibit premelting order/disorder transitions, the reversal of the slope of $\alpha(T)$ normally occurs at the melting point. Furthermore, these materials often exhibit a discontinuity (in several cases a significant drop) in thermal diffusivity at T_m (e.g. alkali metals, Cu, Au), whereas in those which previously undergo

a premelting order/disorder transition the thermal diffusivity mostly increases continuously across the melting point.

A full discussion of these phenomena is outside the scope of this letter; however, some conclusions can be drawn concerning the observed behaviour of $\alpha(T)$ in UO_2 at temperatures above the λ transition. Actually, this transition appears to be an important discriminating feature for several physical properties, which, in the interval between T_c and T_m, are affected by the anion-sublattice disorder to an extent which has not been fully appreciated†. It is, therefore, not surprising that thermal diffusivity is so much affected by oxygen lattice defects that under conditions of pronounced oxygen disorder created by the λ transition this quantity exhibits a temperature dependence which is typical for most glassy structures, whose passage from solid to liquid state occurs without solution of continuity in their dynamical properties. In this context, the thermal diffusivity value obtained by Tasman, and plotted in figure 3, conforms with the observed behaviour of a set of analogous solid and fluid systems and, therefore, appears to be the correct one.

References

[1]   Kim C S, Haley R A, Fischer J, Chasanov M G and Leibowtiz L 1977 *Proc. 7th Symp. on Thermophysical Properties* ed A Cezairliyan (New York: American Society of Mechanical Engineers) pp 338–43
[2]   Otter C and Damien D 1984 *High Temp.–High Pressures* **16** 1–6
[3]   Tasman H A, Pel D, Richter J and Schmidt H E 1983 *High Temp.–High Pressures* **15** 419–31
[4]   Fink J K and Leibowitz L 1984 *High Temp.–High Pressures* **17** 17–26
[5]   Tasman H A 1988 Thermal conductivity of liquid UO_2 *Commission of the European Communities, Joint Research Centre Annual Report* TUAR88 (Karlsruhe, Germany)
[6]   Otter C and Vandevelde J 1982 *Rev. Int. Hautes Temp. Refr. Fr.* **19** 41–53
[7]   Ronchi C and Sari C 1974 *J. Nucl. Mater.* **50** 91–7
[8]   Ronchi C, Hiernaut J P, Selfslag R and Hyland G J 1993 *Nucl. Sci. Eng.* **113** 1–19
[9]   Hiernaut J P, Hyland G J and Ronchi C 1993 *Int. J. Thermophys.* **14** 259–83
[10] Ronchi C and Hyland G J 1994 *J. Alloys Compounds* at press
[11] Hagrman O L 1979 *US Department of Energy Report* EG&G-CDAP 3029 (Idaho Operation Office, Idaho National Engineering Laboratory)
[12] Hyland G J 1983 *J. Nucl. Mater.* **113** 125
[13] Matzke H J 1986 *Adv. Ceram.* **17** 1–54

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† For instance, there is experimental evidence that in UO_2 also cation mass transport coefficients and mechanical properties are affected by the λ transition [13].