AN OVERVIEW OF THE MEASUREMENTS OF THERMOPHYSICAL PROPERTIES AND SOME RESULTS ON MOLTEN SUPERALLOYS AND SEMICONDUCTORS

by

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This presentation consists of two parts: (1) comments on the results of measurements on thermophysical properties based on the paper, "Things Mother Never Taught Me (about Thermophysical Properties of Solids)" and (2) results of thermophysical property measurements on selected solid and molten semiconductors and a proprietary superalloy. The first part may be considered as a tutorial for those involved in using or procuring thermophysical property data. The second part is presented as illustrations of what has been accomplished on molten materials at the Thermophysical Properties Research Laboratory (TPRL). The materials include Ge, PbTe, PbSnTe, HgCdTe and a superalloy.

TPRL operates in two modes of operation: graduate level fundamental studies and contract research. As a result of over 30 years of operation, a number of important lessons were learned. These include the fact that all physical properties are interrelated, that thermal conductivity is difficult to determine accurately and that the literature is full of poor results obtained by researchers who had unwarranted faith in their results. Part of
this faith was usually based on the fact that standards were measured and good results were obtained. It was not understood that this is a necessary, but not sufficient condition to obtain reliable results on unknowns, since auxiliary conditions such as softness, emissivity, ability to attach temperature sensors, etc. must also be taken into account.

Thermal diffusivity values for molten semiconductors were obtained using the laser flash technique. Modifications were made in order to contain molten materials. Results were obtained on a number of semiconductors, including Ge, PbSnTe and Hg$_x$Cd$_{1-x}$Te.

In the case of superalloys, the vapor pressure of constituents such as chromium that have high vapor pressures in the molten region requires that the diffusivity measurements be performed on samples under inert atmosphere (or else sealed samples). The arrangement utilized is indicated in a figure. The sample is contained within a sapphire cup. There is a sapphire lid with spacers that rests on top of the sample. When the sample melts some of it can flow past the spacer. The sample thickness is in melt is controlled by the sapphire cup and top. When the sample solidifies, it sometimes generates enough stress to crack the spacer. The purposes of the spacer is as an expendable piece to protect the relatively expensive sapphire top. The laser pulse passes through the sapphire top to heat the top surface of the sample. The resulting rear face temperature rise is obtained by means of an i.r. detector viewing the bottom surface. Since the heat pulse is applied to the top surface, convection is minimized. Thermal diffusivity results are shown in a figure. Measurements in
the solid region were made using the convectional horizontal furnace and the vertical furnace. The diffusivity values exhibit only a change of slope upon melting, even though the apparent specific heat shows a large increase. When one removes the energetics from the apparent specific heat, the calculated thermal conductivity values follow the trend expected from electrical resistivity considerations. The electronic component is calculated using the classical value for the Weidemann-Franz-Lorenz ratio and as such is known to be about 10% smaller than the total thermal conductivity since thermal and electrical conductivities were measured on the solid sample up to 600°C using the Kohlrausch technique. These total thermal conductivity values lie on the same curve as those calculated from diffusivity/specific heat determinations. Note that specific heat determinations made elsewhere by levitation calorimeter are in error by more than 300%.
Lesson 1:

Properties are Inter- and Intra-Related and are Non-Denominational
(1) $\lambda_e = L_0 T/\rho$ (Thermal-electrical)

(2) $\lambda_p = 1/3C_v \nu \lambda$ (Thermal-mechanical)

(3) $\varepsilon(0, T) = 0.578 \rho T^{1/2} - 0.178 \rho T$
   $+ 0.0514 \rho T^{3/2}$ (Radiative-electrical)

(4) $Y = 2G(1 + \nu)$ Mechanical-chemical bonding
   $\nu = 0.25$ Ionic or Van der Waal bonding
   $\nu < 0.25$ Covalent bonding
   $\nu > 0.25$ Metallic or elastic bonding

(5) $C_p - C_v = B_v^2 TV/\chi$ (Thermal-mechanical)

Lesson 3:

Thermal conductivity is difficult to measure accurately

"DIRECT" measurement involves determining $T$, $\Delta T$, $Q$
Lesson 4:
Reference materials and standards for methods ARE VERY DANGEROUS
Thermal Conductivity of Tungsten

Flash Diffusivity (Schematic)
On-Line Comparison of Experimental Rise curve to Theoretical Model

### TABLE 2

**COMPUTER OUTPUT FOR DIFFUSIVITY EXPERIMENT**  
(F142GG2 at 313 K)

<table>
<thead>
<tr>
<th>Sample: F142GG2</th>
<th>Temp: 1.627 MV = 313 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max: 5.40477 Volts</td>
<td>Halfmax: 3.56397 Volts</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ALPHA \ (cm²/sec)</th>
<th>PER \ (%)</th>
<th>VALUE \ (Volts)</th>
<th>TIME \ (Seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8292</td>
<td>20</td>
<td>2.57695</td>
<td>0.023793</td>
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<tr>
<td>0.8315</td>
<td>25</td>
<td>2.75369</td>
<td>0.026113</td>
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<tr>
<td>0.8313</td>
<td>30</td>
<td>2.93043</td>
<td>0.028989</td>
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<tr>
<td>0.8374</td>
<td>33.3</td>
<td>3.04826</td>
<td>0.029275</td>
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<tr>
<td>0.8291</td>
<td>40</td>
<td>3.28391</td>
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<td>50</td>
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<td>0.049997</td>
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<td>4.34434</td>
<td>0.054109</td>
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<tr>
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<td>75</td>
<td>4.52106</td>
<td>0.058326</td>
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<tr>
<td>0.8389</td>
<td>80</td>
<td>4.69782</td>
<td>0.065112</td>
</tr>
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</table>
Schematic of Laser Flash for Molten Semiconductors
Thermal Diffusivity of Four Ge Samples Showing Effects of Melting, Super-Cooling and Cooling

Thermal Diffusivity of Three Samples of PbSnTe
Thermal Diffusivity of Hg$_x$Cd$_{1-x}$Te $(0.00 \leq x \leq 0.107)$

Schematic of Laser Flash Diffusivity Apparatus for Molten Superalloys
Details of Sample Holder for Molten Alloys

Thermal Diffusivity of Two Samples of a Proprietary Superalloy using both Horizontal and Vertical Furnaces
Specific Heat of a proprietary Superalloy
(Note values Obtained by Levitation are in error by 300%)

Thermal Conductivity of a Proprietary Superalloy
(Values Indicated by Curves Designated by MEAS CP are valid to 800°C and Those Designated by MP and CALC CP are valid above 800°C)