

$$\Gamma_v = \frac{C_g}{C_p} \Gamma_g + \frac{C_e}{C_p} \Gamma_e + \frac{C_m}{C_p} \Gamma_m \quad (5)$$

where the subscripts g, e and m refer to the lattice, electronic and magnetic contributions respectively. In most metals  $\Gamma_g$  varies with temperature with values varying from 1.5 to 3. At low temperature, where  $C_e$  and  $C_m$  may be relatively large, a negative  $\Gamma_v$  and therefore a negative  $\alpha_v$  may arise, as in the case of uranium below 45° K, from the  $\Gamma_e$  and/or  $\Gamma_m$  contributions. Because of the absence of compressibility values below 42° K we cannot at the present time evaluate  $\Gamma_v$  in this interesting temperature range. The other anomaly,  $\alpha_2$  above 350° K, can, however, be analyzed quantitatively using the tensor form of the Grüneisen relation to determine whether a negative  $\Gamma_v$  is necessarily involved in this situation<sup>14</sup>). The following relations are thus obtained:

$$\begin{aligned} \frac{V}{C_p} \alpha_1 &= (s_{11} \Gamma_1 + s_{12} \Gamma_2 + s_{13} \Gamma_3) = \\ &= \frac{\Gamma_1}{E_1} - \frac{\sigma_{21}}{E_2} \Gamma_2 - \frac{\sigma_{31}}{E_3} \Gamma_3 \\ \frac{V}{C_p} \alpha_2 &= (s_{12} \Gamma_1 + s_{22} \Gamma_2 + s_{23} \Gamma_3) = \\ &= -\frac{\sigma_{12}}{E_1} \Gamma_1 + \frac{\Gamma_2}{E_2} - \frac{\sigma_{32}}{E_3} \Gamma_3 \\ \frac{V}{C_p} \alpha_3 &= (s_{13} \Gamma_1 + s_{23} \Gamma_2 + s_{33} \Gamma_3) = \\ &= -\frac{\sigma_{13}}{E_1} \Gamma_1 - \frac{\sigma_{23}}{E_2} \Gamma_2 + \frac{\Gamma_3}{E_3}, \end{aligned} \quad (6)$$

which reduces to,

$$\alpha_v = \frac{C_p}{V} (\beta_{[100]} \Gamma_1 + \beta_{[010]} \Gamma_2 + \beta_{[001]} \Gamma_3). \quad (7)$$

$\Gamma_1$ ,  $\Gamma_2$  and  $\Gamma_3$  are the Grüneisen coefficients which apply for uniaxial thermal strains in the [100], [010] and [001] directions respectively and the same subscript scheme applies to  $E_1$ ,  $E_2$  and  $E_3$ . The solutions for  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma_3$  and  $\Gamma_v$  obtained from the simultaneous equations using the  $s_{ij}$  values from the present measurements, the  $\alpha_i$  computed by Lloyd *et al.*<sup>13</sup>) and the total  $C_p$ <sup>7</sup>) are shown in the curves of fig. 9. All of the  $\Gamma_j$  rise quite sharply upon cooling below 100° K;  $\Gamma_v$  is relatively independent of temperature between 75° K and 700° K, with

a value of 2.35 and decreases to 2.15 at 900° K.  $\Gamma_1$  varies from 2.68 to 2.81 in this range and  $\Gamma_3$  undergoes the greatest changes with limits of 2.45 and 2.97.  $\Gamma_2$  is remarkably constant between 175° K and 300° K and decreases from 1.6 to 1.15 above 300° K. Although the decrease in  $\Gamma_2$  may be a contributing factor, the negative  $\alpha_2$  arises, primarily, from the abnormally large Poisson's ratio  $\sigma_{32}$  and the large negative temperature dependence of  $E_3$ .

#### 4.2. THE ANOMALOUS SPECIFIC HEAT

Fig. 10 shows the temperature dependence of various contributions to the total specific heat for alpha uranium. The  $C_p$  curve between 0° and 300° K is that given by Flotow and Lohr<sup>15</sup>) and the higher temperature part is due to Ginnings *et al.*<sup>7</sup>). The specific heat at constant volume,  $C_v$ , was derived using the thermodynamic relation

$$C_v = \left( \frac{\beta_v}{\alpha_v^2 VT + \beta_v C_p} \right) C_p^2, \quad (8)$$

at temperature  $T$ . The lattice specific heat that was calculated from the Debye model using  $\theta_D$  of 200° K<sup>16</sup>) is noted as the dashed line,  $C_D$ . The experimental lattice specific heat due to temperature change only,  $C_v(V_0, T) - \gamma_0 T$ , was computed from the  $C_v$  data by assuming a temperature independent electronic specific heat coefficient,  $\gamma_0 = 26 \times 10^{-4}$  cal/mol·deg<sup>2</sup><sup>16</sup>); and then correcting for the change in  $C_v$  with volume using the relation

$$\left( \frac{\partial C_v}{\partial V} \right)_T = T \frac{\{\beta_v(d\alpha_v/dT) - \alpha_v(d\beta_v/dT)\}}{V^2} \frac{C_v}{C_p}. \quad (9)$$

The resulting curve approaches the  $C_D$  curve in the range of 100° to 120° K. Below 100° K the specific heat in excess of  $C_D$  increases with decreasing temperature; this reflects either a decreasing  $\theta_D$  or an increasing contribution from the free electrons, or from a magnetic moment. Above 120° K the  $C_v(V_0, T) - \gamma_0 T$  curve follows the Debye function reasonably well, allowing for experimental error, up to approximately 400° K where it has a significant positive curvature and increases above 3  $R$  at higher temperatures.