(6)

nd the anomalous above 350° K⁷). neasurements the t 41° K was esw anomalies that will attempt here di data with the sion and specific sible relationship nd high tempera-

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mperature of the 935° K) the three 1, α_2 and α_3 (sub-[100], [010] and normally affected α_1 decreases with minimum in the ases continuously 100° and 935° K. t 50° K, decreases eximately 350° K tive temperature catures. α_3 has a ture dependence, nost five between

ic moduli on the can be illustrated on:

(4)

ansion coefficient, ant pressure, V is e adiabatic comis the Grüneisen resent case, may volume of 1. the mal modes of the usity of electronic and 3. the energy ese contributions n the basis of the butions:

$$\Gamma_{\rm v} = \frac{C_{\rm g}}{C_{\rm p}} \, \Gamma_{\rm g} + \frac{C_{\rm e}}{C_{\rm p}} \, \Gamma_{\rm e} + \frac{C_{\rm m}}{C_{\rm p}} \, \Gamma_{\rm m} \,. \tag{5}$$

where the subscripts g, e and m refer to the lattice, electronic and magnetic contributions respectively. In most metals Γ_{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 $\Gamma_{\rm v}$ and therefore a negative α_v may arise, as in the case of uranium below 45° K, from the $\Gamma_{\rm e}$ and/or $\Gamma_{\rm m}$ contributions. Because of the absence of compressibility values below 42° K we cannot at the present time evaluate $\Gamma_{\rm v}$ in this interesting temperature range. The other anomaly, α_2 above 350° K, can, however, be analyzed quantitatively using the tensor form of the Grüneisen relation to determine whether a negative $\Gamma_{\rm v}$ is necessarily involved in this situation ¹⁴). The following relations are thus obtained:

$$\begin{split} \frac{V}{C_{\rm p}} \alpha_1 &= (s_{11} \varGamma_1 + s_{12} \varGamma_2 + s_{13} \varGamma_3) = \\ &= \frac{\Gamma_1}{E_1} - \frac{\sigma_{21}}{E_2} \varGamma_2 - \frac{\sigma_{31}}{E_3} \varGamma_3 \\ \frac{V}{C_{\rm p}} \alpha_2 &= (s_{12} \varGamma_1 + s_{22} \varGamma_2 + s_{23} \varGamma_3) = \\ &- \frac{\sigma_{12}}{E_1} \varGamma_1 + \frac{\Gamma_2}{E_2} - \frac{\sigma_{32}}{E_3} \varGamma_3 \\ \frac{V}{C_{\rm p}} \alpha_3 &= (s_{13} \varGamma_1 + s_{23} \varGamma_2 + s_{33} \varGamma_3) = \\ &- \frac{\sigma_{13}}{E_1} \varGamma_1 - \frac{\sigma_{23}}{E_2} \varGamma_2 + \frac{\Gamma_3}{E_3}, \end{split}$$

which reduces to,

$$\alpha_{\mathbf{v}} = \frac{C_{\mathbf{p}}}{V} (\beta_{[100]} \Gamma_1 + \beta_{[010]} \Gamma_2 + \beta_{[001]} \Gamma_3).$$
(7)

 Γ_1 , Γ_2 and Γ_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 Γ_1 , Γ_2 , Γ_3 and Γ_v obtained from the simultaneous equations using the s_{ij} values from the present measurements, the α_i computed by Lloyd *et al.*¹³) and the total C_p^7) are shown in the curves of fig. 9. All of the Γ_j rise quite sharply upon cooling below 100° K; Γ_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. Γ_1 varies from 2.68 to 2.81 in this range and Γ_3 undergoes the greatest changes with limits of 2.45 and 2.97. Γ_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 Γ_2 may be a contributing factor, the negative α_2 arises, primarily, from the abnormally large Poisson's ratio σ_{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 Lohr¹⁵) and the higher temperature part is due to Ginnings *et al.*⁷). The specific heat at constant volume, C_v , was derived using the thermodynamic relation

$$C_{\mathbf{v}} = \left(\frac{\beta_{\mathbf{v}}}{\alpha_{\mathbf{v}}^2 \, VT + \beta_{\mathbf{v}} C_{\mathbf{p}}}\right) C_{\mathbf{p}}^2,\tag{8}$$

at temperature *T*. The lattice specific heat that was calculated from the Debye model using $\theta_{\rm D}$ of 200° K ¹⁶) is noted as the dashed line, $C_{\rm D}$. The experimental lattice specific heat due to temperature change only, $C_{\rm v} (V_0, T) - \gamma_0 T$, was computed from the $C_{\rm v}$ data by assuming a temperature independent electronic specific heat coefficient, $\gamma_0 = 26 \times 10^{-4}$ cal/mol·deg² ¹⁶); and then correcting for the change in $C_{\rm v}$ with volume using the relation

$$\left(\frac{\partial C_{\mathbf{v}}}{\partial V}\right)_{T} = T \frac{\left\{\beta_{\mathbf{v}}(\mathrm{d}\alpha_{\mathbf{v}}/\mathrm{d}T) - \alpha_{\mathbf{v}}(\mathrm{d}\beta_{\mathbf{v}}/\mathrm{d}T)\right\}}{V^{2}} \frac{C_{\mathbf{v}}}{C_{\mathbf{p}}}.$$
 (9)

The resulting curve approaches the $C_{\rm D}$ curve in the range of 100° to 120° K. Below 100° K the specific heat in excess of $C_{\rm D}$ increases with decreasing temperature; this reflects either a decreasing $\theta_{\rm D}$ or an increasing contribution from the free electrons, or from a magnetic moment. Above 120° K the $C_{\rm v}(V_0, T) - \gamma_0 T$ 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.

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