LETTER TO THE EDITOR

Thermal expansion and elastic constants of single-crystalline UPt₃

A de Visser, J J M Franse and A Menovsky
Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Received 19 November 1984

Abstract. Thermal expansion measurements have been performed on single-crystalline UPt₃ between 1.4 and 100 K. Spin-fluctuation terms dominate the volume expansion at low temperatures. The linear terms in the thermal expansion and the specific heat are compared and a giant value is obtained for the appropriate Grüneisen parameter. The elastic constants of UPt₃ at room temperature have been determined from sound velocity measurements. A value of 0.48 Mbar⁻¹ results for the nearly isotropic compressibility.

The coexistence of large anisotropic spin-fluctuation effects and superconductivity in the intermetallic compound UPt₃ is an intriguing phenomenon that attracts much attention. Evidence for spin fluctuations is derived from a pronounced $T^3 \ln(T/T^*)$ term in the specific heat that is only weakly field dependent (Frings et al 1983, Stewart et al 1984, de Visser et al 1984a, b). Measurements of the magnetisation (Frings et al 1983, Franse 1983a, b), magnetoresistivity (Franse et al 1984a, de Visser et al 1984c) and electrical resistivity (de Visser et al 1984d) once more underline the anomalous low-temperature behaviour of this compound. Experiments on single crystals of UPt₃ (hexagonal, MgCd₃-type structure) reveal large anisotropies in the electronic and magnetic properties.

Superconductivity in UPt₃ was first observed by Stewart et al (1984). Meissner effect studies, performed by Palstra et al (1984), prove that superconductivity is a bulk property, although not more than 30% of the full Meissner effect could be observed at 350 mK because of flux-pinning effects. In view of the large electronic coefficient in the specific heat, $\gamma = 422 \text{ mJ (mol F}_{U} \text{)}^{-1} \text{ K}^{-2}$, UPt₃ is classified as a heavy fermion superconductor. Analysing the data on the upper critical field de Visser et al (1984a, b) obtained a value for the effective mass of the pairing electrons of about $180m_e$. The intimate interplay of spin fluctuations and superconductivity in UPt₃ has led to speculations on unconventional triplet pairing in the superconducting state (Varma 1984, Anderson 1984, Bishop et al 1984).

Up to now, evidence for spin fluctuations has mainly been obtained from the specific heat data. The electronic term in the specific heat is enhanced due to scattering of the electrons at the Fermi surface on the spin fluctuations. At temperatures well below a characteristic temperature $T^*$ this is reflected in a $T^3 \ln(T/T^*)$ contribution (Doniach and Engelsberg 1966). From the numerical analysis of the specific heat data (Stewart et al 1984, de Visser et al 1984a, b, Frings 1984) it can be concluded that this temperature dependence holds remarkably well.
We expect a similar temperature behaviour for the thermal expansion. However, the evaluation of the appropriate terms using proper Grüneisen relations is not unambiguous. Therefore, we restrict ourselves in the following numerical analysis to the linear term, dominant for $T$ approaching zero. Neglecting the enhancement due to the electron–phonon interaction, we write in analogy to the specific heat, $C = \gamma_0 (1 + \lambda_s) T$, for the volume expansion $a_s = 3a_0 (1 + \lambda'_s)$, where $\gamma_0$ and $3a_0$ are the usual electronic coefficients and $\lambda_s$ and $\lambda'_s$ are the enhancement factors due to spin fluctuations. Following Fawcett et al. (1970), it can be shown that the enhancement of the thermal expansion for $T$ approaching zero should be more pronounced than that of the specific heat, approximately in the ratio

$$\frac{\lambda'_s}{\lambda_s} = 1 + \frac{1}{\Gamma^0_s} \ln S \frac{\partial \ln S}{\partial \ln V}. \quad (1)$$

Here $\Gamma^0_s = 3a_0 V_m/\kappa\gamma_0$ is the unenhanced electronic Grüneisen parameter and $\partial \ln S/\partial \ln V$ is the relative volume dependence of the exchange enhancement factor $S$; the enhancement factor $\lambda'_s$ is proportional to $\ln S$ according to theory. Using the definition $\chi = S \chi_{Pauli}$, the relative volume dependence of $S$ can be written as

$$\partial \ln S/\partial \ln V = - \partial \ln \chi/\partial P - \Gamma^0_s. \quad (2)$$

Since the pressure dependence of the susceptibility is known from recent experiments, $\partial \ln \chi/\partial P = -24\text{ Mbar}^{-1}$ (Franse et al 1984b, Willis et al 1984) and the compressibility could be determined from the elastic constants, $\kappa = 0.48\text{ Mbar}^{-1}$, we can give an estimate for the enhancement ratio. Inserting the theoretical value of $\frac{1}{2}$ for $\Gamma^0_s$ for $f$ electrons and $S = 5.80 \times 10^6 \chi/\gamma = 1.5$ (Franse 1983b) in equation (1), we obtain the huge enhancement ratio $\lambda'_s/\lambda_s = 51$. Even with the much larger value of $S$ of 34.6 that follows from recent band calculations by Strange and Gyorffy (1984), we calculate an enhancement ratio of seven. Clearly $\lambda'_s$ is one order of magnitude larger than $\lambda_s$.

In order to clarify the effect of spin fluctuations on the thermal expansion, another well known spin-fluctuation compound, UAl$_2$ (Trainor et al 1975), was also measured. Using literature data for $\partial \ln \chi/\partial \ln P$ and $\kappa$ of $-16 \text{ Mbar}^{-1}$ and $1.1 \text{ Mbar}^{-1}$ respectively (Fournier and Beille 1979) and a value of $S$ of 2.3 (Franse 1983b), we estimate the enhancement ratio for this compound at 12.

In the following paragraphs we first describe the experimental details, followed by the experimental results and the analysis. Finally, we discuss the determination of the elastic constants.

A single-crystalline batch of UPt$_3$ was prepared in a tri-arc melting apparatus by the Czochralski method (Menovsky and Franse 1983). A polycrystalline UAl$_2$ sample was prepared by arc melting and subsequently annealed at 800 °C for a period of 10 d. Samples were machined by means of spark erosion into the proper shape, i.e. a $5 \times 5 \times 5 \text{ mm}^3$ cube for UPt$_3$ and a cylinder with $l = 5 \text{ mm}$ and plane parallel surfaces for UAl$_2$. For the thermal expansion measurements a sensitive three-terminal capacitance method was used, with a detection limit for changes in length of 0.1 Å. Data were gathered stepwise: below 15 K each temperature step ($\approx 0.3$ K) was made three times, i.e. up, down and up again, whereas above 15 K only steps upwards were made (up to 3 K). The accuracy in the results decreased with increasing temperature due to small temperature gradients over the cell, and is limited to $3 \times 10^{-7} \text{ K}^{-1}$ in $\alpha$ near 100 K.

The thermal expansion results, obtained in several runs, are presented in figure 1. Up to 100 K the thermal expansion coefficient, $\alpha$, of UPt$_3$ is anisotropic. At 100 K $\alpha$ reaches a value between 8 and $9 \times 10^{-6} \text{ K}^{-1}$, which points to a dominating lattice contribution in this temperature region. The maximum in the plot of $\alpha$ against $T$ for the basal plane
Figure 1. Linear thermal expansion coefficient, $\alpha = (1/L) \frac{dL}{dT}$, along different crystallographic directions for single crystalline UPt$_3$ (□, a; O, b; △, c; +, $\frac{1}{2}\alpha_v = \frac{1}{2}(\alpha_a + \alpha_b + \alpha_c)$) and polycrystalline UAl$_2$ (×).

directions roughly coincides with the maximum in the susceptibility, 16 K (Frings et al. 1983), that was interpreted as a spin-fluctuation phenomenon. In a plot of the volume expansion, $\alpha_v$, this maximum remains clearly visible (figure 1). Comparing our recent results with previous measurements on a polycrystalline sample (de Visser and Franse 1984), we conclude that preferred orientations were present in this polycrystalline sample. At lower temperatures an anomaly in $\alpha$ of UAl$_2$ is present.

In analogy to the specific heat we plot the thermal expansion data as $\alpha/T$ against $T^2$ in figure 2 (note that the maximum at 10 K for UPt$_3$ is obscured in this plot). For both compounds the anomalous behaviour at low temperatures becomes visible as a pronounced upturn. The enhanced electronic coefficient $a_0(1 + \lambda'_e)$ for UPt$_3$ amounts to $1.2 \times 10^{-6}$ K$^{-2}$ approaching 0 K. This means a considerable enhancement when compared with a usual value for the electronic coefficient, $a_0$, of the order of $10^{-8}$ K$^{-2}$. Assuming $\gamma_0 = 225$ mJ (mol FU$^{-1}$) K$^{-2}$ (Frings 1984) we calculate $a_0 = 2 \times 10^{-8}$ K$^{-2}$ from $\gamma_0(1 + \lambda'_e) = \frac{1}{2}$ and subsequently $\lambda'_e = 60$ (see table 1). With $\lambda_v = 0.88$ (the enhanced $\gamma$ value, $\gamma_0(1 + \lambda_v)$, is 422 mJ (mol FU$^{-1}$) K$^{-2}$) we obtain an enhancement ratio $\lambda'_e/\lambda_v$ of 68. Comparing this value with the one that was obtained from equation (1), $\lambda'_e/\lambda_v = 51$, we conclude that the analysis of the specific heat and thermal expansion data under the assumptions given above is quite satisfying. Inserting the experimentally observed
enhancement ratio, 68, in equation (1) would result in a Stoner factor, $S$, of 1.4, in close agreement with the value given above. To bring the enhancement ratio derived from the specific heat and thermal expansion data into agreement with the one calculated from equation (1), $\lambda''/\lambda_0 = 51$, we have to assume a somewhat lower value of $\gamma_0$ of 156 mJ (mol Fu)$^{-1}$ K$^{-2}$, which results in values for the enhancement factors $\lambda_0$ and $\lambda''_0$ of 1.67 and 85, respectively. The enhanced Grüneisen parameter, $\Gamma_{\text{enh}}^{\text{ph}} = 3a_0\lambda''_0 V_m/\gamma_0\lambda_0 = (\lambda''_0/\lambda_0)\Gamma_0^0$, amounts to the giant value 159. Such a large Grüneisen parameter, connecting

Table 1. Electronic ($\gamma_0$) and phonon ($\beta$) coefficients from a two-parameter fit to the specific heat data, $C = \gamma_0 T + \beta T^3$, in the temperature range 15–20 K (Frings 1984), together with enhanced $\gamma$ values, $\gamma_0(1 + \lambda_0)$, and enhanced $a$ values, $a_0(1 + \lambda_0)$, as derived from experiment for temperatures approaching 0 K. The unenhanced electronic ($a_0$) and phonon ($b$) coefficients in the linear thermal expansion coefficient were calculated from the Grüneisen relations, $\lambda''_0 = 3a_0V_m/\gamma_0 = \frac{1}{3}$ and $\lambda''_\text{ph} = 3bV_m/\kappa \beta = 2$, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$\gamma_0$ (mJ (mol Fu)$^{-1}$ K$^{-2}$)</th>
<th>$\gamma_0(1 + \lambda_0)$ (mJ (mol Fu)$^{-1}$ K$^{-2}$)</th>
<th>$\lambda_0$</th>
<th>$\beta$ (mJ (mol Fu)$^{-1}$ K$^{-4}$)</th>
<th>$\theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$\text{Pt}_3$</td>
<td>225</td>
<td>422</td>
<td>0.88</td>
<td>0.85</td>
<td>210</td>
</tr>
<tr>
<td>U$\text{Al}_2$</td>
<td>52</td>
<td>132</td>
<td>1.54</td>
<td>0.65</td>
<td>208</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ ($10^{-8}$ K$^{-2}$)</th>
<th>$a_0(1 + \lambda'_0)$ ($10^{-8}$ K$^{-2}$)</th>
<th>$\lambda'_0$ ($10^{-11}$ K$^{-4}$)</th>
<th>$b$ ($10^{-11}$ K$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U$\text{Pt}_3$</td>
<td>1.98</td>
<td>120</td>
<td>60</td>
<td>6.3</td>
</tr>
<tr>
<td>U$\text{Al}_2$</td>
<td>1.24</td>
<td>36</td>
<td>28</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 2. The linear thermal expansion coefficient $\alpha (= \frac{1}{3}\alpha_v)$ for U$\text{Pt}_3$ where $\alpha_v$ is the volume expansion coefficient) plotted as $\alpha/T$ against $T^2$. □, U$\text{Pt}_3$; ○, U$\text{Al}_2$. 
Table 2. Sound velocities and elastic constants of UPt$_3$ at room temperature. For the calculation of $c_{13}$ we refer to McSkimin (1955). $c_{12} = 1.421$ Mbar follows from a combination of $c_{11}$ and $c_{66}$. $V_8$ served as a cross check. The $c_{ii}$ values are based on the calculated density $\rho = 1.940 \times 10^4$ kg m$^{-3}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of mode</th>
<th>Direction of propagation</th>
<th>Direction of particle motion</th>
<th>Velocity (m s$^{-1}$)</th>
<th>Elastic constant (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>longitudinal</td>
<td>c</td>
<td>c</td>
<td>$v_1 = 3860$</td>
<td>$c_{33} = \rho v_1^2 = 2.891$</td>
</tr>
<tr>
<td>I</td>
<td>shear</td>
<td>c</td>
<td>in ab plane</td>
<td>$v_2 = 1385$</td>
<td>$c_{44} = \rho v_2^2 = 0.372$</td>
</tr>
<tr>
<td>I</td>
<td>longitudinal</td>
<td>$b$</td>
<td>$b$</td>
<td>$v_3 = 3993$</td>
<td>$c_{11} = \rho v_3^2 = 3.093$</td>
</tr>
<tr>
<td>I</td>
<td>shear</td>
<td>$b$</td>
<td>$a$</td>
<td>$v_4 = 2076$</td>
<td>$c_{66} = \frac{1}{2}(c_{11} - c_{12}) = \rho v_4^2 = 0.836$</td>
</tr>
<tr>
<td>I</td>
<td>shear</td>
<td>$b$</td>
<td>$c$</td>
<td>$v_5 = 1388$</td>
<td>$c_{44} = \rho v_5^2 = 0.374$</td>
</tr>
<tr>
<td>II</td>
<td>quasi-longitudinal</td>
<td>$b'$</td>
<td>$b'$</td>
<td>$v_6 = 3754$</td>
<td>$c_{13} = 1.732$</td>
</tr>
<tr>
<td>II</td>
<td>quasi-shear</td>
<td>$b'$</td>
<td>$c'$</td>
<td>$v_7 = 1827$</td>
<td>$c_{13} = 1.695$</td>
</tr>
<tr>
<td>II</td>
<td>shear</td>
<td>$b'$</td>
<td>$a' = a$</td>
<td>$v_8 = 1753$</td>
<td>$\frac{1}{2}c_{11} - \frac{1}{2}c_{12} + \frac{1}{2}c_{44} = \rho v_8^2$</td>
</tr>
</tbody>
</table>

the spin-fluctuation phenomena in the specific heat and thermal expansion data, possibly explains why the anomaly near 10 K in $\alpha$, of UPt$_3$ has not been observed in the specific heat data. A similar analysis for UA$_{12}$, assuming $\gamma_0 = 52$ mJ (mol F.U.$)^{-1}$ K$^{-2}$, leads to the enhancement ratio 18 and a value of $\Gamma^{\text{enh}}$ of 42 (see table 1).

The remaining part of this Letter deals with the elastic properties of UPt$_3$ at room temperature. To determine the five independent elastic constants (hexagonal symmetry) we followed the approach of McSkimin (1955). For these measurements we used conventional ultrasonic equipment, with quartz transducers tuned at 20 MHz (longitudinal waves) and 5 MHz (transverse waves). Two single-crystalline samples, from the same batch as prepared for the thermal expansion sample, were machined into the proper form by means of spark erosion. One sample (I) served for propagation directions along the $c$ axis ($l = 7$ mm) and $b$ axis ($l = 5$ mm). The other sample (II) was shaped for a propagation direction at 45° between the $b$ and $c$ axes, but perpendicular to the $a$ axis. The formulae for the elastic constants are listed in table 2, together with the experimental results. The accuracy in the $c_{ii}$ values is 1%, except for $c_{13}$ in which case it is 3%. The longitudinal sound velocity along the $c$ axis, $v_1 = 3860$ m s$^{-1}$, agrees with the value $3.9 \times 10^5$ cm s$^{-1}$ given recently by Bishop et al. (1984) in their report on ultrasonic attenuation experiments below 1 K.

Using the relations in the paper of McSkimin (1955) we calculate the linear compressibility to be 0.16 Mbar$^{-1}$ in the basal plane and 0.15 Mbar$^{-1}$ along the hexagonal axis. Apparently the compressibility is nearly isotropic. The volume compressibility, $\kappa$, reaches a value of 0.48 Mbar$^{-1}$, which fits in between the values for uranium, 0.99 Mbar$^{-1}$, and platinum, 0.38 Mbar$^{-1}$. Finally the Debye temperature, $\theta_D$, was determined from the elastic constants (see, e.g., Alers 1965), resulting in the value 217 K. This value nearly coincides with the value of 210 K obtained from the low-temperature specific heat analysis of Frings (1984), indicating that the elastic properties of UPt$_3$ do not change significantly while going from room temperature down to liquid-helium temperatures.

In summary we conclude that the thermal expansion of UPt$_3$ and UA$_{12}$ reveals pronounced spin-fluctuation contributions at low temperatures. The numerical analysis of the linear terms in the specific heat and thermal expansion data points to giant electronic Grüneisen parameters, $\Gamma^{\text{enh}}$, amounting to 159 and 42 for UPt$_3$ and UA$_{12}$, respectively.
An explanation of the large anisotropy in UPt$_3$ and the maximum in $\alpha$, near 10 K in terms of crystalline field effects, with the first excited level at approximately 20 K, such as was observed in hexagonal PrNi$_3$ (Lüthi and Ott 1979) for instance, does not seem to be justified by the upturns in the $\alpha/T$ and $C/T$ curves at low temperatures. Thermal expansion data on isostructural non-magnetic compounds are not yet available.

We wish to thank E Louis for experimental assistance and are grateful to T M van Soest for technical assistance and hospitality at the Laboratory for Metal Research of the Technical University of Delft while performing the ultrasonic measurements. This work was part of the research program of the Stichting FOM (Foundation for Fundamental Research of Matter).

References

Anderson P W 1984 *Phys. Rev. B* 30 1549
Donaich S and Engelsberg S 1966 *Phys. Rev. Lett.* 17 750
Fournier J M and Beille J 1979 *J. Physique Coll.* 40 C4 145
Frisings P H 1984 *Thesis* University of Amsterdam
Lüthi B and Ott H R 1979 *Solid State Commun.* 33 717
Menovsky A and Franse J J M 1983 *J. Crystal Growth* 65 286
Strange P and Gyorffy B L 1984 *Proc. Conf. on Electronic Structure and Properties of RE and Actinide Intermetallics, St Pölten (Physica B to be published)*
Trainor R J, Brodsky M B and Culbert H V 1975 *Phys. Rev. Lett.* 34 1019
Varma C M 1984 to be published
de Visser A et al 1984c to be published