Physica B 154 (1989) 379–389
North-Holland, Amsterdam

# GRÜNEISEN ANALYSIS OF SPECIFIC HEAT AND THERMAL EXPANSION OF HEAVY-FERMION $UPt_3$

J.J.M. FRANSE, M. VAN SPRANG, A. DE VISSER* and P.E. BROMMER
*Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands*

Received 1 November 1988
Revised manuscript received 14 November 1988

Existing thermal-expansion and specific-heat data below 35 K for the heavy-fermion superconducting compound $UPt_3$ have been analysed by means of Grüneisen relations. The heavy-fermion contribution to both quantities has been separated in this way from the remaining terms. This analysis has been extended up to 300 K by performing thermal-expansion measurements up to 300 K and combining these results with recent specific-heat data. The entropy associated with the heavy-fermion contribution saturates above 100 K and almost exactly reaches a value of $R \ln 2$ near room temperature. The relative volume change associated with the heavy-fermion state equals $0.9 \times 10^{-3}$.

## 1. Introduction

Among the heavy-fermion superconductors $CeCu_2Si_2$, $UBe_{13}$ and $UPt_3$, the latter compound shows an exceptional temperature dependence of its resistivity: quadratic at the lowest temperatures and saturating for temperatures above 100 K at values between 200 and 300 $\mu\Omega$ cm [1–3]. The other two compounds exhibit typical features of Kondo behaviour with increasing resistivity values for decreasing temperatures down to the point where coherence starts. Similar types of resistivity curves can be observed in the $UPt_3$ system at partly replacing platinum by palladium [4]. However, in the pseudo-binary $U(Pt, Pd)_3$ alloys, superconductivity is rapidily lost and compounds with 0.5 at% Pd do not show a transition anymore down to 40 mK [5]. Instead, long-range antiferromagnetic order develops around 5 at% Pd with values for $T_N$ below 6 K. This long-range antiferromagnetic order, in which uranium moments of the order of $0.6\mu_B$ are involved [6], does not destroy the heavy-fermion state as specific-heat measurements down to 1.4 K indicate [7]. The specific heat of the pure $UPt_3$ compound is also exceptional in the sense that, in contrast to the other heavy-fermion compounds, an analytical expression consisting of terms linear and cubic in temperature with an additional $T^3 \ln T/T^*$-term, represents the specific-heat data over a wide temperature range almost perfectly [8]. This logarithmic term is believed to support a description of $UPt_3$ in terms of spin fluctuations. The Fermi-liquid approach to $UPt_3$ is also largely based on this additional logarithmic term. Apart from the specific-heat experiments, the thermodynamic properties of $UPt_3$ have also been studied in thermal-expansion studies [9]. Roughly speaking, the thermal expansion reflects the volume derivative of the coefficients of the different terms in the specific heat. Giant values have been deduced in this way for the relative volume derivatives of the coefficients that are related to the heavy-fermion state. These results have been verified by measuring the specific heat of $UPt_3$ directly under high pressures [10]. Nevertheless, a three-parameter fit of the volume thermal expansion to the above-introduced analytical expression did not have the same quality as the one for the specific heat. Values for the coefficients turned out to depend strongly on the chosen temperature interval [3] and only below 5 K a satisfying fit is obtained. Recently, a new interpretation of the specific heat of $UPt_3$ has been

* Present address: CRTBT-CNRS BP 166X, F-38042 Grenoble, France.

proposed by Renker et al. [11] in which the electronic part of the specific heat at low temperatures is ascribed to a Kondo anomaly with in addition a crystal-field term. The authors admitted that this interpretation remains strongly hypothetical since a quantitative evaluation of the specific heat data could not be presented due to the large error bars in the electronic part of the specific heat above 20 K.

In the present paper we shall make use of existing specific heat and thermal expansion data of De Visser et al. below 35 K for a single-crystalline sample [8, 9] and combine these results by so-called Grüneisen relations. We shall extend this analysis up to temperatures of 300 K by combining the specific heat data of Felten [12] with the thermal expansion results of Van Sprang et al. [13]. In this latter case we work with results from different groups that have been obtained on samples of different origin. The results of the analysis of these two different sets of data turn out to be consistent. Our analysis is of a thermodynamic nature and is based on the assumption that the different contributions to the entropy are a function of $T/T_j(V)$, i.e. each of the contributions to the free energy is characterised by a single characteristic temperature.

## 2. Grüneisen parameters

In order to relate the volume thermal expansion to the specific heat, so-called Grüneisen parameters are introduced [14]. Physically meaningful Grüneisen parameters emerge if the entropy, or rather a part of the entropy, can be written as $S_j(T/T_j(V))$, where $T_j(V)$ is a volume-dependent, characteristic temperature, like $T_F$ or $\Theta_D$, the Fermi temperature of the electron gas or the Debye temperature, respectively. The dimensionless Grüneisen parameter is defined by

$$\Gamma_j \equiv \frac{V(\partial S_j/\partial V)_T}{T(\partial S_j/\partial T)_V} = -\frac{\mathrm{d}\ln T_j}{\mathrm{d}\ln V}\,, \tag{1}$$

or in terms of the free energy $F_j$ by

$$\Gamma_j = \frac{V(\partial^2 F_j/\partial V\,\partial T)}{T(\partial^2 F_j/\partial T^2)_V}\,. \tag{2}$$

Since the volume expansion coefficient $\beta_j$ is given by

$$\beta_j = \frac{1}{V}\left(\frac{\partial V_j}{\partial T}\right)_P = \kappa\left(\frac{\partial S_j}{\partial V}\right)_T = -\kappa\left(\frac{\partial^2 F_j}{\partial V\,\partial T}\right) \tag{3}$$

(with $\kappa$ the isothermal compressibility) and the specific heat at constant volume $c_j^V$ by

$$c_j^V = T\left(\frac{\partial S_j}{\partial T}\right)_V = -T\left(\frac{\partial^2 F_j}{\partial T^2}\right)_V\,, \tag{4}$$

we derive the following expression:

$$\Gamma_j = \frac{V\beta_j}{\kappa c_j^V}\,. \tag{5}$$

Working with the experimental specific-heat data which have been taken at constant pressure we have to transform the $c_j^P$ data into values for $c_j^V$ according to

$$c_j^V = c_j^P - \frac{TV}{\kappa}\,\beta_j\beta\,. \tag{6}$$

Since $UPt_3$ exhibits large anisotropy effects in the thermal expansion [9], we also investigated the influence of a change in the form. The constant-shape corrections are small compared to the constant-volume corrections and are neglected henceforth. Furthermore the characteristic temperature $T_j$ may depend on the deformation too. Defining the axial deformation $e_{ax}$ as $e_{ax} = 2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{xy}$ $(=2\delta \ln c/a)$, we can repeat the derivation given above, now with $T_j = T_j(V, e_{ax})$. The result is that the same contribution to the specific heat at constant volume and shape, $c_j^{V,e}$, is now related to both the volume thermal expansivity and the axial thermal expansivity, with the appropriate compliance constants and Grüneisen parameters,

$$c_j^{V,e} = \frac{V\beta_j^e}{\Gamma_j\kappa} = \frac{V\beta_{ax,j}^V}{\Gamma_{ax,j}\kappa_{ax}}\,, \quad \Gamma_{ax,j} = \frac{\mathrm{d}\ln T}{\mathrm{d}\,e_{ax}}\,. \tag{7}$$

Notice, however, that a contribution with $T_j =$

$T_j(e)$, independent of the volume, does show up in the specific heat, but not in the volume thermal expansion. In the remaining part of this paper we shall omit the superscript $P$ in referring to the specific heat at constant pressure. If needed, the correction terms between the specific heat at constant volume and shape and at constant pressure will be discussed.

Returning now to our starting assumption we consider the Grüneisen parameter $\Gamma_j$ to be temperature independent. A temperature-independent result, however, can not be expected for the effective Grüneisen parameter $\Gamma_{\text{eff}}$ that is defined by

$$\Gamma_{\text{eff}} = \frac{V\beta}{\kappa c}\,, \tag{8}$$

where

$$\beta = \sum_j \beta_j \quad \text{and} \quad c = \sum_j c_j \tag{9}$$

represent the total thermal expansion and specific heat, respectively.

Apparently:

$$\Gamma_{\text{eff}} = \sum_j \Gamma_j \frac{c_j}{c}\,. \tag{10}$$

In case the different terms $c_j$ have different temperature dependencies and the $\Gamma_j$ have different values, the parameter $\Gamma_{\text{eff}}$ is temperature dependent. On the other hand, a temperature dependence of $\Gamma_{\text{eff}}$ leads to the conclusion that different terms contribute to the thermal expansion and the specific heat or that a scaling of the temperature is not possible in the way indicated above. In case two terms $c_1$ and $c_2$ contribute to the specific heat with the corresponding Grüneisen parameters $\Gamma_1$ and $\Gamma_2$, respectively, we can write

$$\begin{aligned} c_1(T) &= \frac{\Gamma_{\text{eff}}(T) - \Gamma_2}{\Gamma_1 - \Gamma_2}\, c(T)\,, \\ c_2(T) &= \frac{\Gamma_1 - \Gamma_{\text{eff}}(T)}{\Gamma_1 - \Gamma_2}\, c(T)\,. \end{aligned} \tag{11}$$

In a similar way relations can be derived for $\beta_1(T) = \kappa\Gamma_1 c_1(T)/V$ and $\beta_2(T) = \kappa\Gamma_2 c_2(T)/V$. The analysis by means of eq. (11) requires the a priori knowledge of the values for $\Gamma_1$ and $\Gamma_2$. Sometimes, the contributions $c_1(T)$ and $c_2(T)$ dominate in different temperature intervals. An example is the combination of the electronic and phonon terms of a normal metal. At the lowest temperatures the electronic term dominates whereas at high temperatures the phonon term is the larger one. In that case, values for $\Gamma_1$ and $\Gamma_2$ can be deduced in good approximation from the results for $\Gamma_{\text{eff}}(T)$ in the different temperature intervals. Such an analysis has previously been applied to PdMn alloys [15] in order to separate the ferromagnetic and antiferromagnetic contributions and to $ErCu_2$ [16] for splitting the exchange and crystal-field contributions. In general, however, the Grüneisen parameters are not known. Nevertheless, we can calculate, for any choice of $\Gamma_1$ and $\Gamma_2$, the functions $c_1(T)$ and $c_2(T)$, as defined in eq. (11), even in the presence of more than two contributions. In case one Grüneisen parameter (and thus $\Gamma_1$) is much larger than the other ones and the corrsponding contribution ($c_1$) is not exceedingly small, it can easily be shown that the function $c_1(T)$ represents the true contribution $c_1$ very accurately with the exception of the temperature region where $c_1/c$ becomes very small. In the next section we shall apply this analysis to the thermal expansion and specific heat of $UPt_3$. Our choice of $\Gamma_1$ is guided by the maximum value of $\Gamma_{\text{eff}}(T)$, whereas $\Gamma_2$ can be chosen in the neighbourhood of the minimum value of $\Gamma_{\text{eff}}(T)$. To get confidence in the followed procedure we perform it twice: at first by dividing the total specific heat and thermal expansion as measured on a single-crystalline sample by De Visser et al. for temperatures below 35 K in two different contributions characterised by a high (73) and a low (2.35) value for the corresponding Grüneisen parameters. The high value is characteristic for the heavy-fermion state, the low value is mainly determined by the phonon contribution. In a second analysis for temperatures up to 300 K, we subtract the phonon contribution from the measured specific heat and thermal expansion as measured by Felten [12] and by Van Sprang [13],

respectively, and describe the remaining electronic term again with a high (73) and a low (2) value for the Grüneisen parameter. The high value is again related to the heavy-fermion state, the low value in this case to the normal electron gas. In both types of analysis we arrive at nearly identical results for the heavy-fermion contribution to the specific heat and thermal expansion.

## 3. Grüneisen relations applied to $UPt_3$

To start our analysis we make use of published data by De Visser and co-workers for the specific heat and the thermal expansion of single-crystalline $UPt_3$ for temperatures below 35 K [8, 9]. These results are shown in figs. 1a and 1b in plots of $c/T$ and $\alpha/T$ vs. $T$, respectively, where $\alpha$ represents the average of the linear thermal expansion coefficients along the main crystallographic directions: $\alpha = \frac{1}{3}(\alpha_a + \alpha_b + \alpha_c) = \frac{1}{3}\beta$. The temperature dependence of the effective Grüneisen parameter, as defined by eq. (8), is shown in fig. 2. Two temperature regimes can be distinguished in fig. 2: a low-temperature regime in which $\Gamma_{\rm eff}$ approaches a value of 73, and a high-temperature regime in which values below 5 occur. In the high-temperature regime the specific heat turns out to be strongly dominated by the phonons. Appropriate values for the phonon Grüneisen parameter are about 2. In this case we take the value of 2.35 as deduced from the room temperature values of the specific heat and thermal expansion, both after subtracting a small electronic term. In fact we have to consider the corrections to the specific heat at constant volume and shape with respect to the experimentally observed quantity. According to eq. (11), an error $\delta c$ in the specific heat leads to a relative error in $c_1$ of $-(\Gamma_2/\Gamma_{\rm eff})\delta c/c$. The "constant-volume" correction $\delta c = -V\beta^2 T$ leads to a relative error in $c_1$ of magnitude $\Gamma_2 \beta T$, and thus can be seen to be negligibly small. The "constant-shape" correction can be shown to be negligible too. We are now able to split the specific heat and thermal expansion into two different contributions, taking $\Gamma_1 = 73$ and $\Gamma_2 = 2.35$, see figs. 3a and 3b. It is obvious from figs. 3a and 3b that the high-$\Gamma_1$ contribution is dominating in the thermal expansion over the full temperature range 1.5–35 K, whereas in the specific heat this contribu-

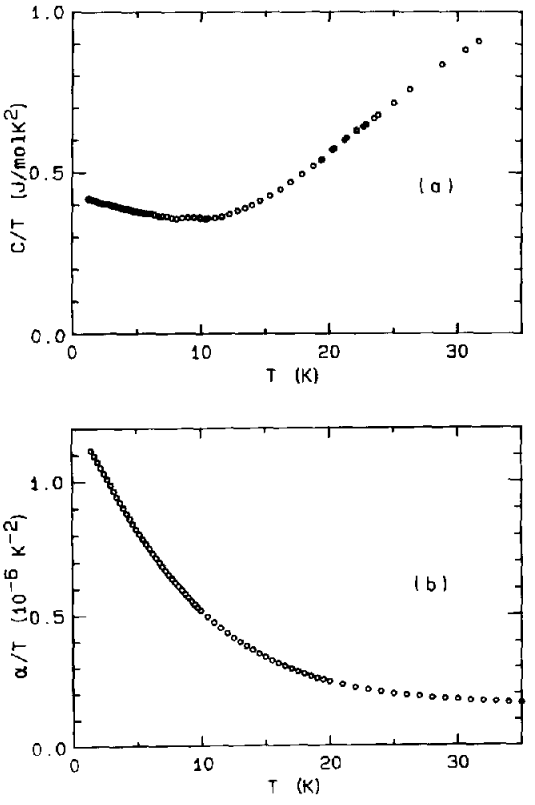



Fig. 1. (a) Specific heat of $UPt_3$ in a plot of $c/T$ vs. $T$; data from ref. [8]. (b) Linear thermal expansion of $UPt_3$ in a plot of $\alpha/T$ vs. $T$, where $\alpha = 1/3(\alpha_a + \alpha_b + \alpha_c) = 1/3\beta$; data from ref. [9].

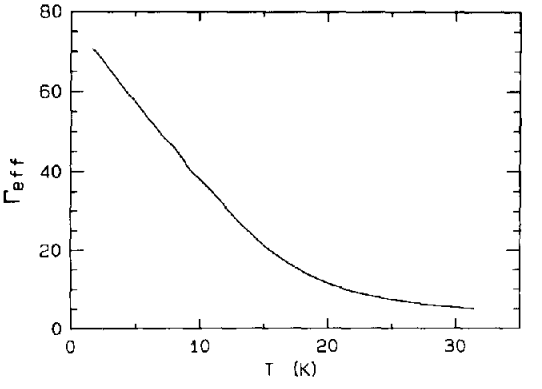
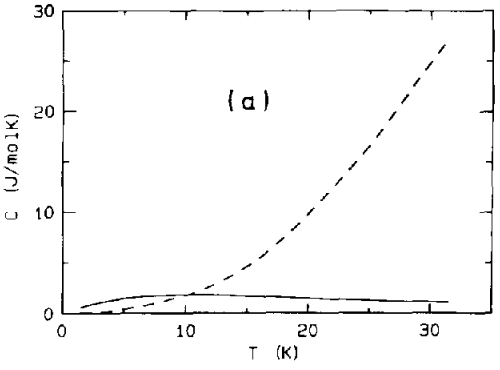



Fig. 2. Temperature dependence of the effective Grüneisen parameter, $\Gamma_{\rm eff} = \beta V_m/\kappa c$, calculated from the data presented in fig. 1.



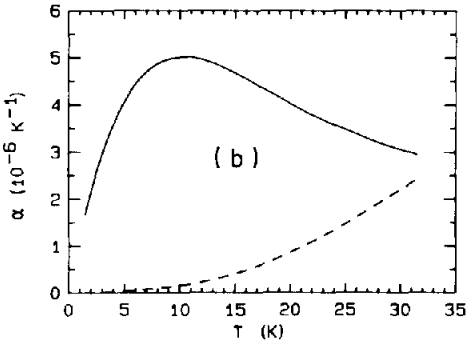




Fig. 3. (a) The specific heat of $UPt_3$, as shown in fig. 1a, split into two contributions $c_1$ (solid curve) and $c_2$ (dashed curve) by means of eq. (11) with values for the corresponding Grüneisen parameters of 73 and 2.35, respectively. (b) The corresponding splitting of the linear thermal expansion, as shown in fig. 1b, into the two contributions $\alpha_1$ (full curve) and $\alpha_2$ (dashed curve).

tion is dominant only below 10 K. This mere fact already explains why a description that is successful for the specific heat, fails for the thermal expansion as we mentioned in the introduction. To get a better insight in the heavy-fermion term, we plot in fig. 4 the term $c_1$ vs. log $T$ and include in this figure the result of a Bethe–Ansatz solution for a Kondo doublet [17, 18], where the maxima of $c_1$ and the Kondo-term have been chosen at the same temperature. In order to let the Kondo-term better represent the specific-heat data at the lowest temperatures we have to shift the Kondo-curve to lower temperatures. Such a procedure is similar to the procedure followed by Renker et al. [11]. The second term in the specific heat, $c_2$, is shown in fig. 5

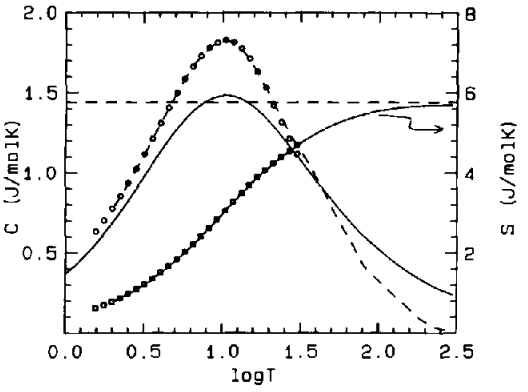



Fig. 4. The heavy-fermion contribution $c_1$ to the specific heat of $UPt_3$ according to a Grüneisen analysis of the specific-heat and thermal-expansion data below 35 K, plotted versus log $T$. Open circles: the low-temperature data for $c_1$. Squares: the corresponding values for the entropy. Curves through the data points: a high-temperature analysis of the electronic part of the specific heat. Full curve: a spin $-1/2$ Kondo-type of contribution to the specific heat.

and compared with the phonon contribution as deduced from the phonon-dispersion curves determined by Renker et al. [19]. Apart from the phonon contribution there is an additional term present in $c_2$, that in the interpretation scheme of Felten resembles a crystal-field contribution. The temperature dependence of this additional term as well as the entropy that is involved in this term give no convincing proof for this interpretation. The additional term critically depends on the exact shape of the phonon contribution and

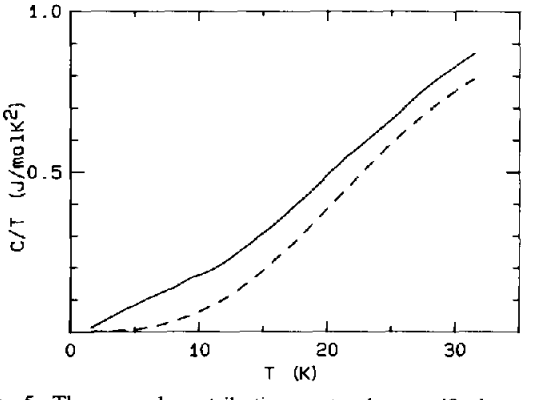



Fig. 5. The second contribution $c_2$ to the specific heat of $UPt_3$ (solid curve) according to a Grüneisen analysis of the specific-heat and thermal-expansion data below 35 K. The phonon contribution according to ref. [19] is indicated by the dashed line.

on the choice for $\Gamma_1$. We shall return to this discussion later. At this point we like to emphasise that in our Grüneisen analysis there is no presumption about the nature of the heavy-fermion term. Just by applying this Grüneisen analysis we arrive at a temperature dependence of the heavy-fermion contribution to the specific heat that shows some similarities with the hypothetical model of Renker et al. [11]. The overall shape of the $c_1$ vs. log $T$ curve, however, differs from the calculated Kondo term by its increased maximal value and by its reduced width. The entropy that is involved with this term approaches the relevant value of $R \ln 2$.

In our second approach we combine the high-temperature specific-heat data reported by Felten [12] and the high-temperature thermal-expansion data obtained by De Visser et al. [9] and by Van Sprang et al. [13]. The thermal-expansion data are shown in fig. 6. These specific-heat and thermal-expansion results have been obtained from different samples. The phonon contribution to the specific heat has been evaluated by Felten on the basis of the neutron scattering results of Renker et al. [19]. Representing the phonon contribution by a Debye function one has to conclude that below 20 K the Debye temperature rapidly increases with decreasing temperatures from a value of 200 K around and above 20 K to a value of 320 K at the lowest temperatures. This variation in the Debye temperature may be accompanied by a variation in the phonon Grüneisen parameter in this temperature interval. According to eq. (11) we derive $\mathrm{d} \ln c_1 / \mathrm{d} \ln \Gamma_2 = -4 \times 10^{-2}$ at 10 K, indicating that a variation of $\Gamma_2$ has a minor effect on the value of $c_1$ around this temperature. The phonon contribution to the thermal expansion has been calculated with a Debye function with $\theta_D = 200$ K, assuming a value for the appropriate Grüneisen parameter $\Gamma^{ph}$ of 2.35. This value emerges from a comparison of the overall results for the specific heat at constant volume and the coefficient of thermal expansion at constant pressure at room temperature, taking into account an electronic contribution to both quantities with a value of 2 for the corresponding electronic Grüneisen parameter $\Gamma^{el}$. Since the phonon contribution to the thermal expansion below 20 K is relatively small, we did not take into account the variation in $\Theta_D$ below 20 K in the evaluation of the phonon contribution to the thermal expansion. After subtracting the phonon contributions to the specific heat and the thermal expansion we are left with the electronic contribution to both quantities which are shown in figs. 7a and 7b. Due to uncertainties in the phonon contribution, the uncertainty of the electronic term in the specific-heat rapidly increases with increasing temperatures; the error bars in fig. 7a have been taken from the original publication by Felten. They are much smaller in the thermal expansion below 50 K, due to different relative weights of the electron and phonon contributions. Comparing the data in figs. 7a and 7b, we can evaluate the effective electronic Grüneisen parameter $\Gamma^{el}_{eff}$ and deduce a low-temperature limiting value of 73 and a high-temperature limiting value of 2. This temperature dependence of $\Gamma^{el}_{eff}$ suggests at least two contributions to be present: $c^{el} = c^{el}_1 + c^{el}_2$ with values for the corresponding Grüneisen parameters of 73 and 2. We split again $c^{el}$ by means of eq. (11) in $c^{el}_1$ and $c^{el}_2$, and similarly $\alpha^{el}$ in $\alpha^{el}_1$ and $\alpha^{el}_2$, see figs. 8a and 8b. The results for $c^{el}_1$ and its related entropy are represented by the dashed curves in fig. 4. In the overlapping temperature range, perfect agreement with the former analysis is reached.

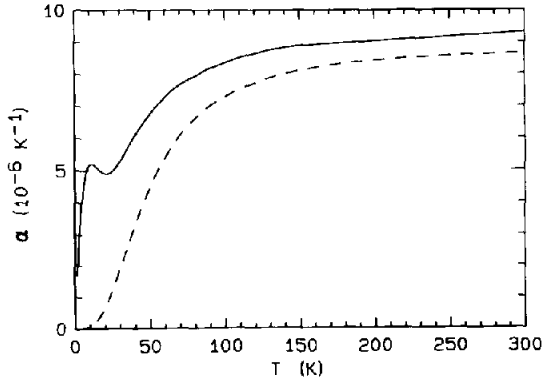



Fig. 6. Linear thermal-expansion data of $UPt_3$ according to De Visser et al. [9] and Van Sprang et al. [13]. The dashed curve represents the phonon contribution calculated with a Debye function with a value for $\Theta_D$ of 200 K and $\Gamma^{ph}$ equal to 2.35.

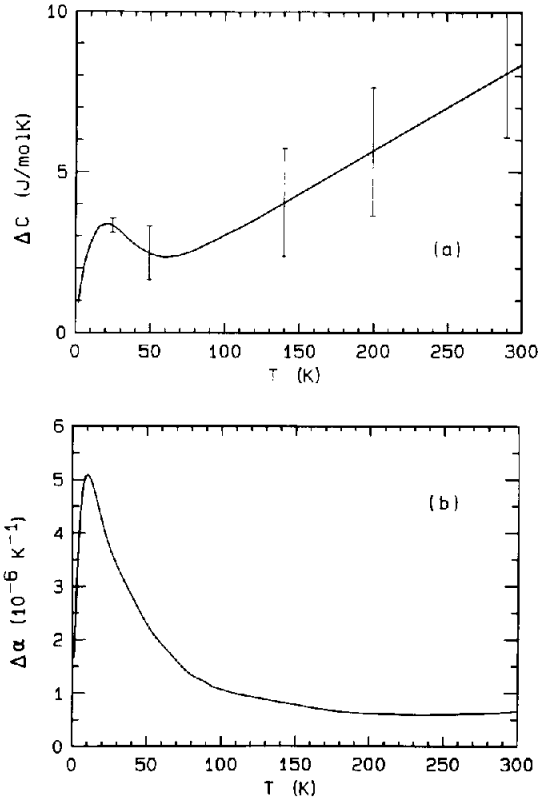



Fig. 7. (a) The electronic contribution to the specific heat of $UPt_3$ after subtracting the phonon contribution from the total specific heat; data and error bars taken from ref. [12]. (b) The electronic contribution to the linear thermal expansion of $UPt_3$ after subtracting the phonon contribution; data from refs. [9] and [13].

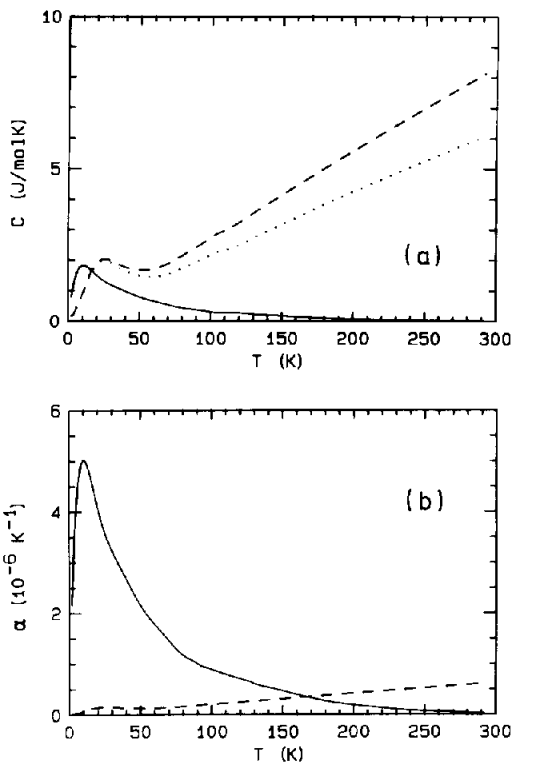



Fig. 8. (a) Splitting of the electronic part of the specific heat into two contributions $c_1^{el}$ and $c_2^{el}$ with corresponding values for the Grüneisen parameters of 73 (solid curve) and 2 (dashed curve), respectively. The dotted curve represents specific-heat data at constant volume for the second contribution $c_2^{el}$. For the first contribution $c_1^{el}$ the data at constant volume coincide with the data at constant pressure. (b) Splitting of the electronic part of the linear thermal expansion into the corresponding contributions $\alpha_1^{el}$ (solid curve) and $\alpha_2^{el}$ (dashed curve).

## 4. Discussion

In the analysis presented above we were able to separate the heavy-fermion part in the specific heat and the thermal expansion from the remaining contributions by applying Grüneisen relations. Two different approaches were followed and in both cases the same results were obtained in the overlapping temperature region. Most satisfactory is the value for the entropy related to the heavy-fermion part in the specific heat that almost exactly equals $R \ln 2$ near room temperature. As we pointed out in the foregoing section, the heavy-fermion part in the specific heat resembles a single-ion spin $-1/2$ Kondo contribution, although there are differences in the maximal value and the peak width. Moreover, a description of the heavy-fermion behaviour of $UPt_3$ in terms of a single-ion Kondo effect neglects the large coherence effects that turn out to be present at low temperatures. At least one point is clarified by our analysis: the almost perfect three-parameter description of the specific heat up to temperatures of 20 K, mentioned in the introduction, no longer contradicts the low value of 29 K for the spin-fluctuation temperature obtained in the same analysis. The good quality of this fit up to such high temperatures is accidental and must be ascribed to a second electronic contribution, possibly of a

crystal-field nature. It is interesting to present the heavy-fermion contribution to the specific heat in a plot of $c/T$ vs. $T$, see fig. 9. The heavy-fermion part is still describable with the sum of two terms: $\gamma^* T$ and $\delta T^3 \ln T/T^*$. The temperature range over which a good-quality fit is obtained is now much more reduced and a similar quality as for the thermal expansion is attained. At the lowest temperatures (1.5–5 K) the following values for the heavy-fermion parameters are obtained: $\gamma^* = 433(422)$ mJ/K$^2$ mol, $\delta = 5.88(1.38)$ mJ/K$^4$ mol and $T^* = 12.4(27)$ K (values between brackets refer to a previous analysis of the total specific heat in the temperature interval 1.4–10 K [8]). The major progress that is realised with the present analysis is not so much a new theoretical interpretation of the heavy-fermion terms in specific heat and thermal expansion as well as a separation of these terms from the remaining contributions over a wide temperature range. We already mentioned the total entropy that is involved in the heavy-fermion contribution to the specific heat. By integrating the heavy-fermion part in the specific heat and in the volume thermal-expansion coefficient we can evaluate the energy and the volume that are associated with the formation of the heavy-fermion state. The energy divided by the Boltzmann constant equals 13 K. The result for the volume is shown in fig. 10.

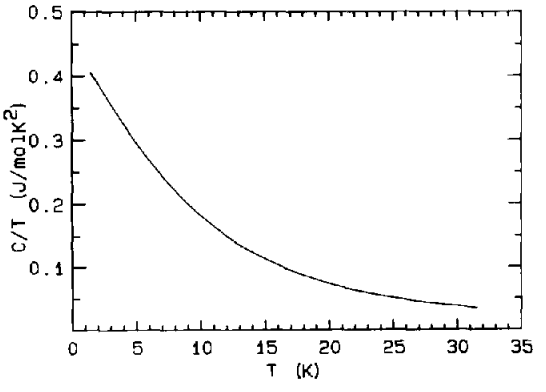



Fig. 9. A plot of $c/T$ vs. $T$ for the heavy-fermion contribution to the specific heat of $UPt_3$ as presented in fig. 3a. A low-temperature (<5 K) fit to the expression $c_1(T) = \gamma^* T + \delta T^3 \ln T/T^*$ results in $\gamma^* = 433$ mJ/mol K$^2$, $\delta = 5.88$ mJ/mol K$^4$ and $T^* = 12.4$ K.

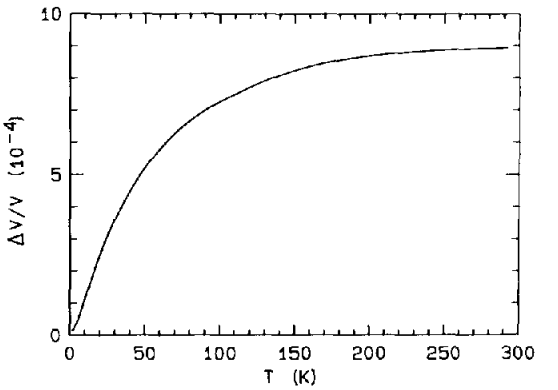



Fig. 10. The temperature dependence of the volume anomaly due to the formation of the heavy-fermion state, calculated by a temperature integration of $3\alpha_1$ with data for $\alpha_1$ as given in fig. 8b.

One way of looking at this result is to consider the volume collapse $\Delta V/V = 0.9 \times 10^{-3}$ as a consequence of the loss of the localised uranium magnetic moment going to low temperatures. In this view we interpret the volume anomaly as a magnetovolume effect. By comparing this volume anomaly with the forced-magnetostriction data at low temperatures of De Visser et al. [20] we are, in principle, able to evaluate a value for the magnetic moment that is associated with it. The low-field (up to several tesla) magnetostriction data at 4.2 K for the field perpendicular to the $c$-axis can be represented by

$$\frac{\Delta V}{V} = \tfrac{1}{2}\, a\, \mu_0^2 H^2 , \tag{12}$$

with a value for the parameter $a$ of $4.61 \times 10^{-7}$T$^{-2}$. This expression can be transformed into a relation between the relative volume change and the field-induced magnetic moment per formula unit:

$$\frac{\Delta V}{V} = C\, \mu_{\mathrm{f.u.}}^2 , \tag{13}$$

with a value for the parameter $C$ equal to $5.81 \times 10^{-4} {\mu_B}^2$ using the magnetisation data for fields applied perpendicular to the hexagonal axis [21]. Applying eq. (13) to the result of $0.9 \times 10^{-3}$ for the relative volume anomaly in the heavy-fermion state, we deduce a value for the high-

temperature moment per formula unit of $1.24\mu_B$. We consider this value as an upper limit for the thus calculated uranium moment. The value of $5.81 \times 10^{-4}\mu_B^{-2}$ for the magneto–volume parameter $C$ has been obtained under the implicit assumption that the low-field susceptibility in the hexagonal plane can be fully ascribed to the heavy-fermion effect. We can not exclude, however, that part of the susceptibility is due to, for instance, an orbital or another normal contribution. By taking the difference in the susceptibility between the hexagonal axis and the hexagonal plane as the heavy-fermion part of the susceptibility we derive the smaller value for the moment per formula unit of $0.6\mu_B$. Since the long-range magnetic moment of the 5 at% $U(Pt, Pd)_3$ alloy amounts to about $0.6\mu_B$/f.u. and this alloy has still to be considered as a heavy-fermion system we prefer to use a larger value than $0.6\mu_B$ for the magnetic moment per uranium atom in the normal state. The forced-magnetostriction data as presented by De Visser et al. [22] for magnetic fields up to 24 T provide another argument that the heavy-fermion state is still present in fields just above the metamagnetic transition at 20 T in the hexagonal plane at temperatures in the liquid helium range. According to these magnetostriction data, the relative increase in volume amounts to $3.1 \times 10^{-4}$ in 24 T at 4.2 K, only 1/3 of the volume anomaly of the heavy-fermion state. A similar increase in volume is found in fig. 10 at a temperature of 26 K, stressing the equivalent role of temperature and magnetic field in depressing the heavy-fermion state. The picture that emerges from this discussion points to a loss of the heavy-fermion state as soon as localised magnetic moments around $1.2\mu_B$ develop on the uranium atoms, suggesting a suppression of the heavy-fermion state in applied magnetic fields well exceeding 100 T.

Forced-magnetostriction measurements [20, 22] as well as high-pressure experiments on the magnetic susceptibility [23] and the resistivity [24, 25] provide additional information on the volume derivative of the characteristic temperature of the heavy-fermion state. Roughly speaking, the value for the relative volume derivative of this temperature as derived in the liquid-helium temperature region from the pressure dependence of the coefficient $A$ in the expression $\rho(T) = \rho_0 + AT^2$, as well as the value derived from the pressure dependence of the susceptibility in the hexagonal plane or from the thermodynamically related forced volume magnetostriction for fields applied in the hexagonal plane, all agree rather well with the large value for this volume derivative as deduced from the value for $\Gamma_1$ of 73 according to eq. (1). The pressure dependence of the susceptibility within the hexagonal plane has been measured as a function of temperature up to 40 K. The pressure-induced shift of the temperature at which this susceptibility reaches its maximal value (around 17 K) results in a value for the logarithmic volume derivative of this temperature of $63 \pm 13$, again a value close to that for $\Gamma_1$, giving support to a description of the heavy-fermion state by one single characteristic temperature. In choosing the value for $\Gamma_1$ equal to $\Gamma_{\text{eff}}$ at the lowest temperatures we implicitly ignored substantial low-temperature contributions to the specific heat from other origins. A neglection of phonon and crystal-field contributions at the lowest temperatures can be justified. We can not a-priori exclude, however, that a normal electronic contribution, linear in temperature, is present. In our choice for $\Gamma_1$ in fact we assume that all electrons at the Fermi surface participate in the heavy-fermion state, an assumption that is consistent with the results of de Haas-van Alphen studies on $UPt_3$ in which large mass enhancements are found for all investigated sheets of the Fermi surface [26].

We finally turn to the second contribution of electronic origin in the specific heat, $c_2^{el}$. At temperatures well above 100 K this contribution seems to be linear in temperature. In fact, especially at high temperatures a more careful analysis is required in which the specific-heat data at constant pressure are transformed according to eq. (6) in specific-heat data at constant volume before subtracting the phonon contribution. Taking these corrections into account, a value for the coefficient of the linear term results, equal to $21 \pm 8$ mJ/mol K$^2$. This value for the coefficient of the linear term is quite close to a value of about 20 mJ/mol K$^2$ that follows from electronic

bandstructure calculations for $UPt_3$ [27–30]. The entropy that is involved with this second electronic contribution equals $9 \pm 3$ J/mol K at 300 K. A rough estimate of the band-electron contribution to this entropy above 100 K results in a value of 6 J/mol K. Ascribing the remaining part in $c_2^{el}$ to crystal-field effects, we must conclude that at most one additional doublet is involved apart from the doublet that is behind the heavy-fermion state. The suggestion that crystal-field effects are visible in $UPt_3$ is mainly based on the analysis of the specific-heat data of Renker et al. [11]. In our own analysis of the specific-heat and thermal-expansion data below 35 K we are, apart from the heavy-fermion contribution with an entropy value of $R \ln 2$, left with a second contribution that is mainly determined by phonons. This second contribution does not follow the phonon term as determined by Renker et al. and definitely contains another term. Whether this additional term is related to the anisotropy in the thermal expansion, to special electron-phonon processes at low temperatures or to crystal-field interactions, remains unsolved.

## 5. Summary

The specific heat and the thermal expansion of $UPt_3$ have been split in different contributions by means of Grüneisen relations. The heavy-fermion part in both quantities has been isolated in this way over a large temperature interval. The entropy involved with the heavy-fermion contribution to the specific heat almost exactly approaches a value of $R \ln 2$ near room temperature, whereas the volume collapse that is associated with the heavy-fermion state leads to a value for $\Delta V/V$ of $0.9 \times 10^{-3}$. The heavy-fermion contribution to the specific heat resembles in some respects a spin $-1/2$ Kondo-type of contribution, although clear-cut differences are present. A description of the electronic part of the specific heat at low temperatures with an additional $T^3 \ln T/T^*$-term is still successful below 5 K and leads to a value for $T^*$ of 12.4 K, close to the temperature where heavy-fermion contributions to specific heat and thermal expansion develop their maxima.

## References


[1] G.R. Stewart, Rev. Mod. Phys. 56 (1984) 755.
[2] U. Rauchschwalbe, Physica B 147 (1987) 1.
[3] A. de Visser, A. Menovsky and J.J.M. Franse, Physica B 147 (1987) 81.
[4] R. Verhoef, A. de Visser, A. Menovsky and J.J.M. Franse, Physica B 142 (1986) 11.
[5] J.J.M. Franse, K. Kadowaki, A. Menovsky, M. van Sprang and A. de Visser, J. Appl. Phys. 61 (1987) 3380.
[6] P.H. Frings, B. Renker and C. Vettier, J. Magn. Magn. Mat. 63 & 64 (1987) 202.
[7] A. de Visser, J.C.P. Klaasse, M. van Sprang, J.J.M. Franse, A. Menovsky, T.T.M. Palstra and A.J. Dirkmaat, Phys. Lett. A 113 (1986) 489.
[8] J.J.M. Franse, P.H. Frings, A. de Visser, A. Menovsky, T.T.M. Palstra, P.H. Kes and J.A. Mydosh, Physica B 126 (1984) 116;
A. de Visser, J.J.M. Franse, A. Menovsky and T.T.M. Palstra, J. Phys. F 14 (1984) L191.
[9] A. de Visser, J.J.M. Franse and A. Menovsky, J. Phys. F 15 (1985) L53.
[10] G.E. Brodale, R.A. Fisher, N.E. Philips, G.R. Stewart and A.L. Giorgi, Phys. Rev. Lett. 57 (1986) 234.
[11] B. Renker, F. Gompf, E. Gering, P. Frings, H. Rietschel, R. Felten, F. Steglich and G. Weber, Physica B 148 (1987) 41.
[12] R. Felten, Thesis, Darmstadt (1987).
[13] M. van Sprang, Thesis, Amsterdam (1989).
[14] P.E. Brommer, Physica B 112 (1982) 343.
[15] P.E. Brommer, J.J.M. Franse, B.M. Geerken, R. Griessen, H. Hölscher, J.A.M. Kragtwijk, J.A. Mydosh and G.J. Nieuwenhuys, Inst. Phys. Conf. Proc. Ser. 55 (1981) 253.
[16] N.H. Luong, J.J.M. Franse and T.D. Hien, J. Magn. Magn. Mat. 50 (1985) 153.
[17] A.M. Tsvelick and P.B. Wiegmann, Adv. Phys. 32 (1983) 453.
[18] V.T. Rajan, Phys. Rev. Lett. 51 (1983) 308.
[19] B. Renker, F. Gompf, J.B. Suck, H. Rietschel and P.H. Frings, Physica B 136 (1986) 376.
[20] A. de Visser, E. Louis, J.J.M. Franse and A. Menovsky, J. Magn. Magn. Mat. 54–57 (1985) 387.
[21] P.H. Frings and J.J.M. Franse, Phys. Rev. B 31 (1985) 4355.
[22] A. de Visser, L. Puech, W. Joss, A.A. Menovsky and J.J.M. Franse, Jap. J. Appl. Phys. 26 (S26-3) (1987) 513.
[23] J.J.M. Franse, P.H. Frings, A. Menovsky and A. de Visser, Physica B 130 (1985) 180.
[24] J.O. Willis, J.D. Thompson, Z. Fisk, A. de Visser,

J.J.M. Franse and A. Menovsky, Phys. Rev. B 31 (185) 1654.
[25] A. Ponchet, J.M. Mignot, A. de Visser, J.J.M. Franse and A. Menovsky, J. Magn. Magn. Mat. 54–57 (1986) 399.
[26] L. Taillefer, R. Newbury, G.G. Lonzarich, Z. Fisk and J.L. Smith, J. Magn. Magn. Mat. 63 & 64 (1986) 372.
[27] P. Strange and B.L. Gyorffy, Physica B 130 (1985) 41.
[28] J. Sticht and J. Kübler, Solid State Commun. 54 (1985) 389.
[29] T. Oguchi and A.J. Freeman, J. Magn. Magn. Mat. 52 (1985) 174.
[30] A.M. Boring, R.C. Albers, F.M. Mueller and D.D. Koelling, Physica B 130 (1985) 171.