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Anisotropy in the thermal expansion of heavy-fermion UPt$_3$ at the superconducting transition

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

K. Hasselbach, A. Lacerda, L. Taillefer, P. Haen, and J. Flouquet
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique,
Boîte Postale 166 X, 38042 Grenoble-CÉDEX, France

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We have measured the coefficients of linear thermal expansion ($\alpha_{\parallel}$ and $\alpha_{\perp}$) of two single-crystalline samples of heavy-fermion UPt$_3$ down to temperatures well below the superconducting transition ($T_c \simeq 0.5$ K). The thermal expansion is strongly anisotropic at T_c, where only $\alpha_{\parallel}$ has a discontinuity. This implies that T_c is suppressed for a uniaxial stress along the hexagonal axis only. In the superconducting phase $\alpha_{\parallel}$ and $\alpha_{\perp}$ vary approximately quadratically, with temperature, as does the specific heat. The Grüneisen parameter shows a large drop at T_c; from 69 in the normal phase to -10 in the superconducting phase.

In the few years that elapsed since the discovery[1] of superconductivity in heavy-fermion UPt$_3$, a wide assortment of experimental and theoretical expertise has been applied to establish that the superconducting condensate is of an unconventional nature. Perhaps the most convincing evidence for unusual superconductivity stems from the observation of a complex phase diagram in the H-T plane, as deduced from ultrasound,[2] mechanical oscillators,[3] and specific-heat experiments[4] performed in an external magnetic field. Moreover, specific-heat data taken on different types of samples clearly resolved the existence of two superconducting phases at zero field.[5,6] From substantial group-theoretical work[7,8] it has been inferred that the multiplicity of superconducting phases is brought about by a coupling of the superconducting and magnetic order parameters. The normal-state magnetic properties of UPt$_3$ are governed by strongly anisotropic antiferromagnetic spin-fluctuation phenomena,[9] but also a weak antiferromagnetic long-range order ($|\vec{\mu}| = 0.02\mu_B$), with a Néel temperature $T_N = 5$ K, is found[10,11] in some of the samples. It has been suggested[7,8] that the symmetry-breaking field, induced by this magnetic order, distorts hexagonal UPt$_3$ and lifts the degeneracy, thus causing the double superconducting transition. Neutron-diffraction experiments[12] have recently provided experimental evidence for such a coupling of the magnetic and superconducting order parameters.

In the quest to further unravel the intriguing properties of superconducting UPt$_3$, it is of interest to study the linear thermal expansion coefficients. Little is known about the thermal expansion of superconductors.[13] Detailed measurements on single-crystalline samples of materials with noncubic symmetry are especially scarce. However, thermal-expansion measurements can be very useful, as, for instance, a combination of specific heat (c) and thermal expansion (α) might provide important information on the (uniaxial) pressure dependence of the superconducting transition temperature (T_c) via the Ehrenfest relation for second-order phase transitions

$$\frac{dT_c}{dP} = \frac{V_m T_c \Delta\alpha_v}{\Delta c_P} . \tag{1}$$

Here $\Delta\alpha_v = \alpha_{vs} - \alpha_{vn}$ and $\Delta c = c_s - s_n$ are the jumps in the coefficient of volume expansion and molar specific heat under constant pressure at T_c, respectively, and $V_m (= 4.25 \times 10^{-5}$ m^3/mol) is the molar volume. Inserting, in the case of UPt$_3$, the values $dT_c/dP = -12.6$ mK/kbar (Ref. 14), $T_c = 0.5$ K, and $\Delta c \simeq 0.1$ J/K mol (Ref. 5), we predict $\Delta\alpha_v \simeq -6 \times 10^{-7}$ K^{-1}. The corresponding jump in the average linear thermal-expansion coefficient amounts to -2×10^{-7} K^{-1}, which is small but experimentally accessible.

The normal-state thermal expansion of UPt$_3$ has been studied[15,16] in the temperature interval $1.4 < T < 300$ K. The coefficients of linear thermal expansion along ($\alpha_{\parallel}$) and at right angles ($\alpha_{\perp}$) to the hexagonal axis reveal a large anisotropy. On heating, the unit cell first contracts along the c axis and expands in the basal plane. Above 45 K both axes dilate. The volume expansion exhibits a broad maximum at 10 K, which is related to the onset of antiferromagnetic intersite correlations.[9]

In this Rapid Communication, we present the first complete set of thermal expansion data of superconducting UPt$_3$. We have studied two single-crystalline samples prepared in different ways. A Czochralski-grown specimen (sample 1) has been prepared by Menovsky in a tri-arc furnace under a gettered argon atmosphere. It has been annealed and shaped by means of spark erosion into a cube with plan parallel surfaces (edge 5 mm), normal to the main crystallographic directions. Sample 2 has been prepared by Taillefer in an induction furnace under ultra-high vacuum. The tiny sample ($3 \times 2 \times 1$ mm^3) was spark-cut from a slowly cooled polycrystalline rod containing large grains. Specific-heat measurements[4,6] on samples cut from the same batches (and correspondingly heat treated) reveal clearly a double superconducting

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transition as shown in Fig. 1. The onset temperature for sample 2 is higher (520 vs 470 mK) and its transition widths are narrower. The splitting into T_{c1} and T_{c2} amounts to 60 mK for both samples.

In order to measure the thermal expansion, $\alpha = L^{-1} \times (dL/dT)$, a sensitive three-terminal capacitance method with a detection limit of 0.1 Å was used. The samples were mounted in a cell made of oxygen-free high-conductivity copper,[17] that was attached to the mixing chamber of a dilution refrigerator. A germanium thermometer and a heater were placed on the cell. The data were gathered stepwise ($\Delta T \gtrsim 5$ mK), allowing the cell to reach thermal equilibrium after each step. The data have been corrected for the cell effect, i.e., the signal of the cell with a copper probe. For a 5-mm sample the correction to α amounts to 1.6×10^{-7} K^{-1} at 1 K, 2.4×10^{-7} K^{-1} at 0.5 K, and 4.6×10^{-7} K^{-1} at 0.1 K. The absolute accuracy amounts to 2×10^{-7} K^{-1}.

The experimental results, obtained after several runs, are shown in Fig. 2 in a plot of α vs T. For sample 1 we present the as-measured data, but for sample 2 a statistical averaging procedure was followed to smooth the data. The volume expansion, $\alpha_v = \alpha_a + \alpha_b + \alpha_c = 2\alpha_\perp + \alpha_\parallel$, has been calculated at selected temperatures after spline-fitting $\alpha_\perp$ and $\alpha_\parallel$. The present results are in good agreement with the previous high-temperature data taken on another unannealed Czochralski-grown sample.[15] In order to compare our data with the specific-heat data of Fig. 1, we have plotted α/T vs T in Fig. 3.

The most striking of our results is the large anisotropy in the anomaly at the superconducting transition. The data in Fig. 3 make it plausible that for an ideal sample $\alpha_\perp$ has a kink and $\alpha_\parallel$ a discontinuity at T_c. However, due to the rather large temperature steps the transitions are somewhat smeared out. Correspondingly, the volume expansion turns up as a broad anomaly. The onset temperatures cannot be determined as accurately as in the $c(T)$ measurements, but amount to 450 and 510 mK for samples 1 and 2, respectively. The T_{c1}'s determined by the midpoint of the transition along the c axis equal 430 and 490 mK, respectively, in agreement with the specific-heat data. No sign of the second superconducting transition at T_{c2} ($=370$ and 430 mK, respectively) has been observed. The experimental accuracy puts an upperbound of $\pm 2\times10^{-7}$ K^{-2} for the anomaly in α/T at T_{c2}.

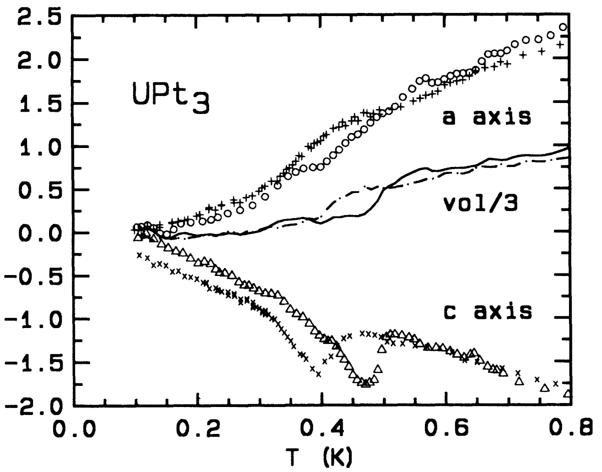

FIG. 2. Coefficient of linear thermal expansion of UPt$_3$ vs temperature along the a and c axes for sample 1 (+,x) and sample 2 (○,Δ). The dashed and solid lines correspond to $\alpha_v/3$ (for samples 1 and 2, respectively).

From Fig. 3 we conclude that $\alpha_\perp$ and $\alpha_\parallel$ exhibit a behavior linear in T above T_c, and close to quadratic below T_c, just as the specific heat (Fig. 1). In the low-temperature limit of the data we observe a finite α_v/T value: $\lim_{T\to0}\alpha_v/T \simeq -1.5\times10^{-6}$ K^{-2}, which is consistent with the observation[5] of a finite γ value, indicating that part of the Fermi surface remains normal. However, the error bar on the low-temperature part of the data is considerable (due to the large cell contribution), and more precise measurements will be needed to detail the behavior below 300 mK. Therefore, we focus in the following on the anomaly at the superconducting transition.

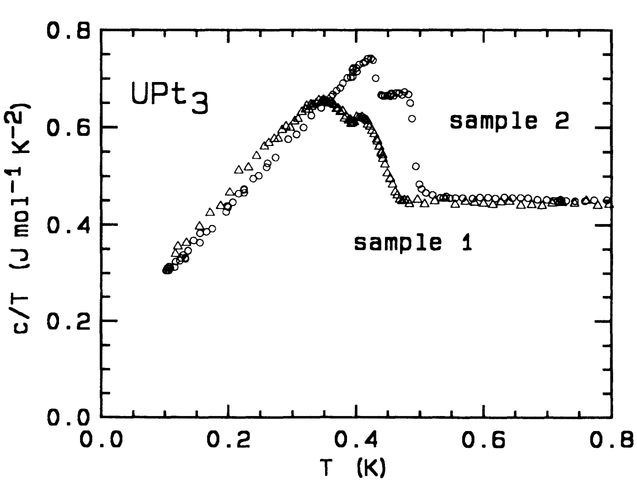

FIG. 1. Specific heat of UPt$_3$ in a plot of c/T vs T for sample 1 (Δ) and sample 2 (○) (after Refs. 6 and 4, respectively).

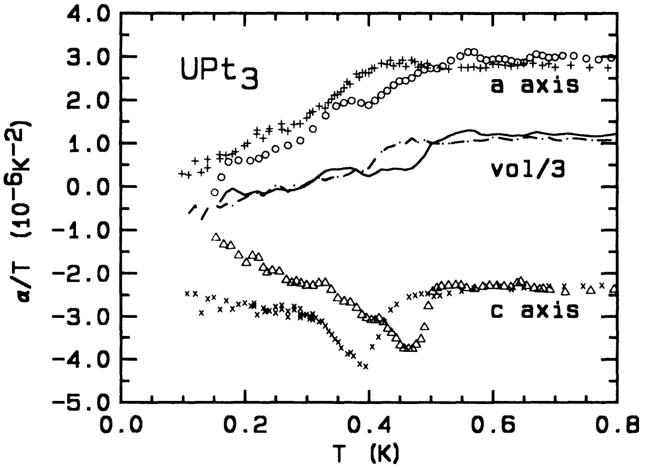

FIG. 3. Coefficient of linear thermal expansion of UPt$_3$ in a plot of α/T vs T, along the a and c axes for sample 1 (+,x) and sample 2 (○,Δ). The dashed and solid lines correspond to $\alpha_v/3$ (for samples 1 and 2, respectively).

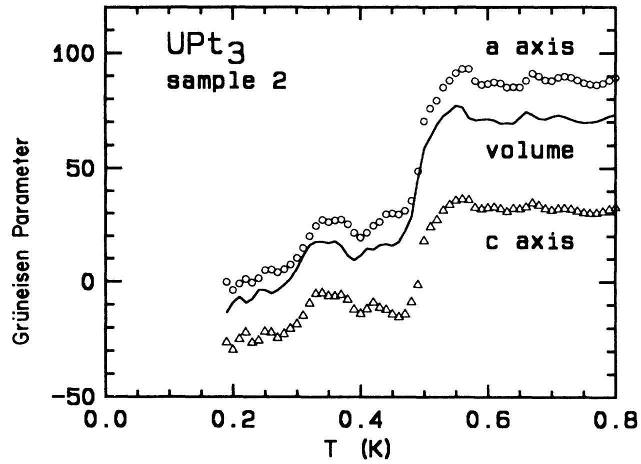

FIG. 4. Volume and directional Grüneisen parameters as a function of temperature for sample 2: Γ_{vol} (solid line), $\Gamma_{\parallel}$ (Δ), and $\Gamma_{\perp}$ (o).

Next we apply the Ehrenfest relation to the upper superconducting transition. Replacing the measured jumps in α_v and c_P with the ideal values obtained in the usual way,[5] we obtain values for Δc of 0.093 and 0.106 J/mol K and values for $\Delta\alpha_v$ of -0.87×10^{-6} and -0.83×10^{-6} K^{-1} at T_{c1} equal to 430 and 490 mK, for samples 1 and 2, respectively. Inserting these values in Eq. (1) we obtain for the variation of T_{c1} with pressure $dT_{c1}/dP = -17$ and -16.3 mK/kbar, respectively. Measurements of the T_c of a whisker as a function of hydrostatic pressure by means of resistivity experiments[18] suggest an initial decrease of $dT_{c1}/dP = -24$ mK/kbar, whereas above 2 kbar dT_c/dP amounts to -13.5 mK/kbar (compared to -12.6 mK/kbar in Ref. 14). The pressure variation of T_{c1} deduced from Eq. (1) should be compared with the initial value obtained from the resistivity experiments, which is about 50% larger.

The anisotropy in the anomaly at the superconducting transition implies that the measured variation of T_c as function of hydrostatic pressure is solely related to the pressure effect on the c axis. A uniaxial pressure along the a axis will not affect T_c. This is consistent with recent uniaxial pressure experiments.[19]

In order to compare the specific-heat and thermal-expansion data, we employ the concept of Grüneisen parameters. The volume Grüneisen parameter is defined by[13]

$$\Gamma_{\text{vol}} = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_{S,P} = \frac{\alpha_v V_m}{\kappa_S c_P}, \tag{2}$$

where κ_S is the adiabatic compressibility ($\kappa_S \simeq \kappa_T$; Ref. 20). Using the data in Fig. 1 and Fig. 3 we have calculated $\Gamma_{\text{vol}}(T)$. The results for sample 2 are shown in Fig. 4. The normal-state Grüneisen parameter attains the huge value of 69, in agreement with previous results.[15,20] Similar large values have been observed for other heavy-fermion compounds, implying a large volume dependence of the quasiparticle bands.[20,21] At the superconducting transition Γ_{vol} shows a dramatic drop and becomes negative below 300 mK. The structure in Γ_{vol} near 400 mK is partly related to the absence of an anomaly at T_{c2} in the thermal-expansion data, but can for the main part be attributed to the scatter in α. More precise data will be needed to discuss these details.

Since hexagonal UPt_3 has strongly anisotropic properties it is more appropriate to utilize directional Grüneisen parameters $\Gamma_{\perp}$ and $\Gamma_{\parallel}$, which are strain derivatives of the entropy[13]

$$\Gamma_{\perp} = \frac{1}{2}\frac{(\partial S/\partial \ln a)c,T}{c_\eta} = \frac{V_m[(c^s_{11}+c^s_{12})\alpha_{\perp}+c^s_{13}\alpha_{\parallel}]}{c_P}, \tag{3}$$

and

$$\Gamma_{\parallel} = \frac{(\partial S/\partial \ln a)a,T}{c_\eta} = \frac{V_m(2c^s_{13}\alpha_{\perp}+c^s_{33}\alpha_{\parallel})}{c_P}. \tag{4}$$

Here c_η is the specific heat under constant strain and the c^s_{ij}'s are the adiabatic elastic constants (c^s_{ij} is within 1% equal to the isothermal elastic constant c^T_{ij}; Ref. 20). Γ_{vol}, $\Gamma_{\perp}$, and $\Gamma_{\parallel}$ are related by $\Gamma_{\text{vol}} = (2\kappa_{\perp}\Gamma_{\perp}+\kappa_{\parallel}\Gamma_{\parallel})/\kappa$, where $\kappa_{\perp} = (-1/a)(da/dP)$ and $\kappa_{\parallel} = (-1/c)(dc/dP)$ are the linear compressibilities[15] and $\kappa = 2\kappa_{\perp}+\kappa_{\parallel}$. Using the room-temperature values[15] for c_{11}, c_{12}, c_{13}, and c_{33}, and neglecting their weak temperature dependence,[20] we have calculated $\Gamma_{\perp}$ and $\Gamma_{\parallel}$. The results for sample 2 are shown in Fig. 4. In the normal state we obtain $\Gamma_{\parallel} = 30$ and $\Gamma_{\perp} = 90$. At the superconducting transition $\Gamma_{\parallel}$ and $\Gamma_{\perp}$ drop sharply. In the low-temperature regime $\Gamma_{\perp}$ extrapolates to a value of ~ 0, indicating that the superconducting properties are rather insensitive to a strain in the basal plane. On the other hand the finite value for $\Gamma_{\parallel}(= -30)$ reflects the strong variation of the superconducting properties for a strain along the c axis.

In conclusion, we have presented the coefficients of linear thermal expansion of UPt_3 in the superconducting phase. The superconducting anomaly turns up as a discontinuity in α along the hexagonal axis and a kink in the basal plane. The analysis implies that the superconducting properties are strongly coupled to a strain or stress along the hexagonal axis, whereas they are rather insensitive for a strain or stress in the basal plane.

Note added in proof. Having increased the temperature resolution and the sensitivity of our dilatometer, we have also detected an anomaly in $\alpha_{\parallel}$ at T_{c2} for sample 2.

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