Thermal expansion and specific heat of monocrystalline URu_2Si_2

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Thermal-expansion and specific-heat measurements have been performed on a monocrystalline sample of URu_2Si_2 in the temperature region between 1.4 and 100 K. The thermal expansion of this tetragonal compound is strongly anisotropic and exhibits several anomalies in the investigated temperature range. Broad anomalies are centered around 5 and 25 K, whereas sharp peaks in the thermal-expansion coefficients are observed at the transition to the antiferromagnetic state at 17.5 K. The c/a ratio exhibits a similar temperature dependence as the susceptibility along the tetragonal axis. The anomaly in the thermal expansion near 25 K suggests the presence of crystal-field effects, in agreement with recent calculations for the magnetic susceptibility at elevated temperatures.

The observation of antiferromagnetic order below 17.5 K and of superconductivity below 1 K (Refs. 1 and 2) brings the compound URu_2Si_2 to the center of discussions concerning the coexistence of magnetic order and superconductivity. Although the magnetic order below 17.5 K is supported by sharp spin-wave excitations, the magnetic moment itself can hardly be detected and has been reported to be as small as $(0.03 \pm 0.02)\mu_B$ per uranium atom and directed along the tetragonal axis.[3] This value of $(0.03 \pm 0.02)\mu_B$ strongly contrasts with values for the magnetic moment per uranium atom of 1.6–$2.9\mu_B$ in other magnetically ordered compounds of the UT_2Si_2 series with T a d transition element.[4,5] High-magnetic-field experiments, however, reveal that a magnetic moment of this order of magnitude is realized for URu_2Si_2 at 1.4 K in a two-step process in fields exceeding 35 T.[6] These results either point to a complex type of antiferromagnetic order, or to fascinating electronic properties that lead to field-induced magnetic moments at 36 and 40 T.

Because of the small values of the magnetic moments below 17.5 K, there is still the question whether the ordering phenomenon at this temperature is of magnetic origin. In case of the compound UPd_3, for instance, the anomalies in the specific heat, that were observed near 6 K, were shown in thermal-expansion measurements to mark a structural transition driven by a quadrupolar ordering.[7] Other suggestions concerning the specific-heat and resistivity anomalies in URu_2Si_2 at 17.5 K refer to an itinerant type of antiferromagnetism[2] or to the opening of an energy gap over part of the Fermi surface in connection with a spin- or charge-density wave.[8]

Although there are no clear-cut predictions for the lattice anomalies in most of the above-suggested descriptions for the phase transition at 17.5 K, thermal-expansion data will undoubtedly contribute to a better understanding of this transition. Referring to the case of UPd_3, a structural transition can be accompanied by anomalies in the thermal-expansion coefficient of the order of 10^{-4}–10^{-5} K^{-1}. A similar order of magnitude has been observed for the peaks in the thermal-expansion coefficient of the antiferromagnetic series RCu_2 (R is a heavy rare-earth metal) with ordering temperatures between 9 and 54 K.[9] On the other hand, anomalies of the order of 10^{-6} have been reported for such a complex magnetic system as UPt (Ref. 10) in which ferromagnetic and antiferromagnetic interactions compete.[11]

A combination of specific-heat and thermal-expansion data offers the possibility to deduce information on the pressure dependence of magnetic and electronic parameters in the temperature region of interest. Such a study on the heavy-fermion compounds, for instance, reveals large values for the electronic Grüneisen parameter, by two orders of magnitude exceeding the free-electron value.[12,13] These large numbers indicate that the thermal-expansion coefficient is much more sensitive to the interactions that cause the heavy-fermion behavior at low temperatures than the specific heat itself. Since URu_2Si_2 is also claimed to belong to the class of heavy-fermion systems, large anomalies can be expected in the thermal expansion of this compound at low temperatures.

High-pressure experiments on a single-crystalline URu_2Si_2 sample reveal a positive pressure dependence of the antiferromagnetic transition temperature: $\Delta T_N/\Delta p = 118$ mK/kbar.[6] According to the thermodynamics of a second-order phase transition, this pressure dependence can be related to the jumps in the specific-heat and the volume thermal-expansion coefficient. This relation serves as a check on the reliability of the different experimental techniques by which the magnetovolume parameters are studied.

The experiments reported in this contribution were performed on a single-crystalline URu_2Si_2 sample, cubic in shape (edge 5.0 mm). The cubic edges are parallel to the main crystallographic directions of the tetragonal com-
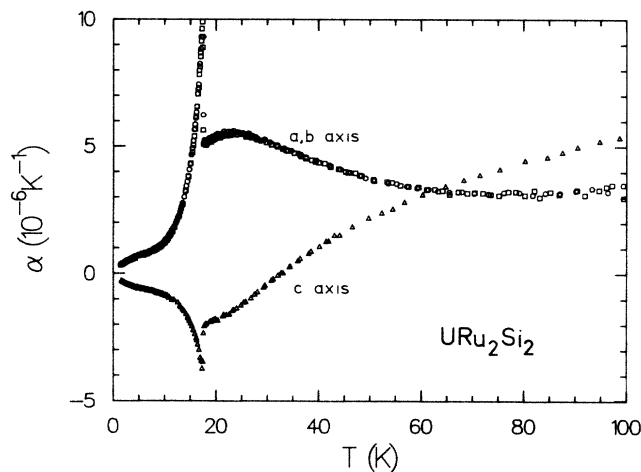
FIG. 1. The thermal-expansion coefficient $\alpha(=L^{-1}\Delta L/\Delta T)$ along the three crystallographic axes of the tetragonal compound URu_2Si_2; a axis (O), b axis (□), c axis (△).

FIG. 3. The c/a ratio of URu_2Si_2 normalized to 1 at 1.4 K, as a function of temperature.

pound ($ThCr_2Si_2$ type of structure). The sample was cut out of a large monocrystalline cylindrical bar, grown by the Czochralski method in a three-arc melting equipment.[14] Parts of this large sample were used in high-field magnetization studies and in high-pressure resistivity measurements.[6] Superconductivity in these samples is found below 1 K.

Thermal expansion was measured by means of a three-terminal capacitance method as described before in connection with experiments on UPt_3.[12] Data were taken along the tetragonal axis and along the two directions in the tetragonal plane at temperatures between 1.4 and 100 K. The specific heat of the same sample was determined by an adiabatic method between 1.2 and 40 K in zero field and in an applied field of 5 T.

An overall picture of the temperature dependence of the thermal-expansion coefficients along the three principal crystallographic directions is presented in Fig. 1 for the
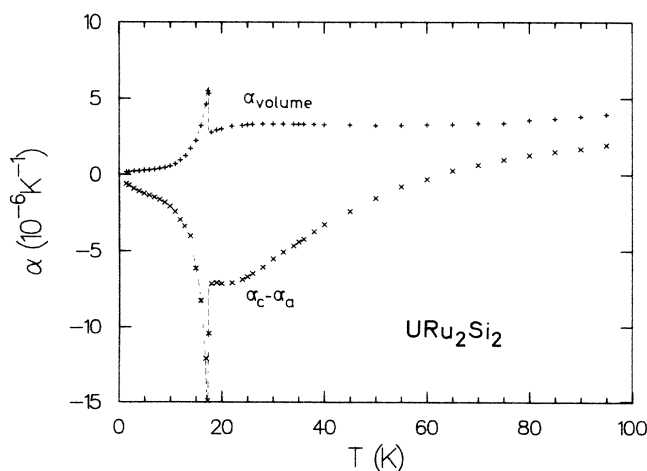
temperature interval between 1.4 and 100 K. From these data the volume expansion coefficient, determined as $\alpha_v = (\alpha_a + \alpha_b + \alpha_c)/3$ and the temperature coefficient of the c/a ratio, given by $\alpha_r = \alpha_c - \alpha_a$, have been calculated; see Fig. 2. In the tetragonal plane no anisotropy is found in the values for the thermal-expansion coefficients. Broad anomalies occur around 5 and 25 K, whereas a sharp peak is observed at the phase transition at 17.5 K. The thermal-expansion coefficient along the tetragonal axis is negative below 30 K and reveals the same type of anomalies as along directions in the tetragonal plane. Above 60 K the thermal-expansion coefficient along the tetragonal axis exceeds those in the tetragonal plane. By integrating the α_r curve of Fig. 2, the temperature dependence of the c/a ratio has been calculated; see Fig. 3. This ratio decreases with increasing temperature and changes in a continuous way around the phase transition at 17.5 K, developing a minimum around 60 K. The specific heat of URu_2Si_2 is shown in Fig. 4 in a plot of c vs T below 40 K. The jumps in the specific-heat and volume thermal-

FIG. 2. The volume thermal-expansion coefficient $\alpha_v = (\alpha_a + \alpha_b + \alpha_c)/3$, and the relative temperature dependence of the c/a ratio $\alpha_r = \alpha_c - \alpha_a$, as determined from the data of Fig. 1; α_v (+), α_r (×).
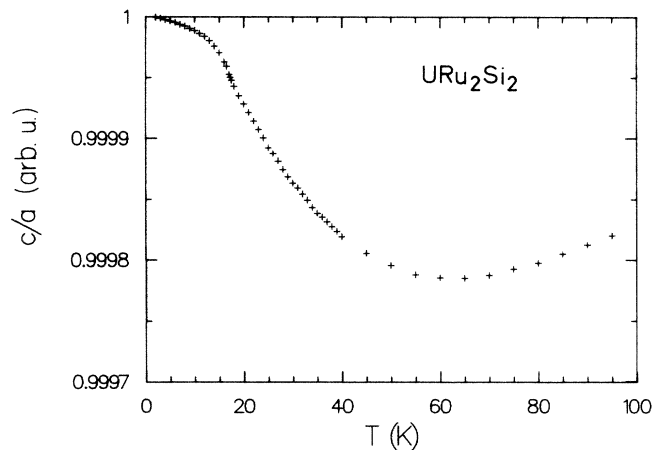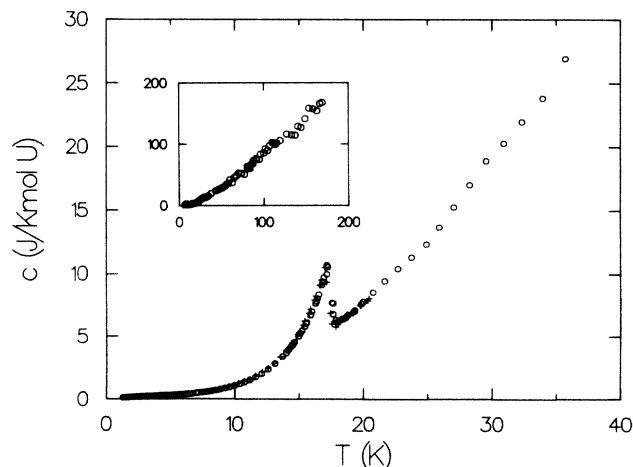

FIG. 4. The specific heat of URu_2Si_2 as a function of temperature in zero field (O) and in 5 T (+). The inset shows the specific heat up to 170 K.

expansion coefficient at the phase transition amount to 5.5 J/K^2 mol and 3×10^{-6} K^{-1}, respectively. Below the phase transition the two curves behave in a rather similar way. The specific-heat and thermal-expansion data below 10 K are shown in Figs. 5 and 6 in a plot of c/T and α_i/T vs T^2, respectively. A small upturn in the c/T and α_v/T values can be observed below 5 K. This upturn is not affected by a field of 5 T. A similar upturn in the specific heat has also been observed in the data reported by Schlabitz *et al.*[1] An extrapolation of the c/T vs T^2 curve to zero temperature, results in a c/T value of 64 mJ/K^2 mol. The corresponding value for α_v/T amounts to 0.8×10^{-7} K^{-2}.

The specific-heat and the volume thermal-expansion coefficient can be approximated at the lowest temperatures by the following expressions: $c = \gamma T$ and $\alpha_v = aT$, respectively. Values for the coefficients γ and a have been given above. These results enable us to deduce a value for the electronic Grüneisen parameter according to the expression $\Gamma_e = 3aV_m/\kappa\gamma$, with V_m the molar volume ($= 4.9 \times 10^{-5}$ m^3/mol) and κ the compressibility. Taking the extrapolated values for the parameters a and γ we calculate a value for $\kappa\Gamma_e$ of 18.4×10^{-11} m^2/N. Since the quantity $\kappa\Gamma_e$ is equal to the relative pressure derivative of the specific-heat coefficient γ we find $\partial\ln\gamma/\partial p = -18.4$ Mbar^{-1}. This result is successively compared with high-pressure data on the susceptibility and the resistivity, which have been reported recently by Louis, de Visser, Menovsky, and Franse.[15] For the tetragonal axis the relative pressure dependence of the susceptibility has been found to be equal to (-29 ± 5) Mbar^{-1}. For the coefficient of the term quadratic in temperature of the resistivity at low temperatures, a value of 0.16 $\mu\Omega$ cm K^{-2} has been obtained with a value for the relative pressure dependence of this parameter of (-48 ± 6) Mbar^{-1}. As in other heavy-fermion systems like UPt$_3$ and UAl$_2$, the parameter $\gamma^2 A$ is almost pressure independent. By lack of information on the compressibility we use a weighted average of the compressibilities of the constituent elements in the solid state and take a value for κ of 0.73×10^{-11} m^2/N. In this way we arrive at a value for the Grüneisen parameter
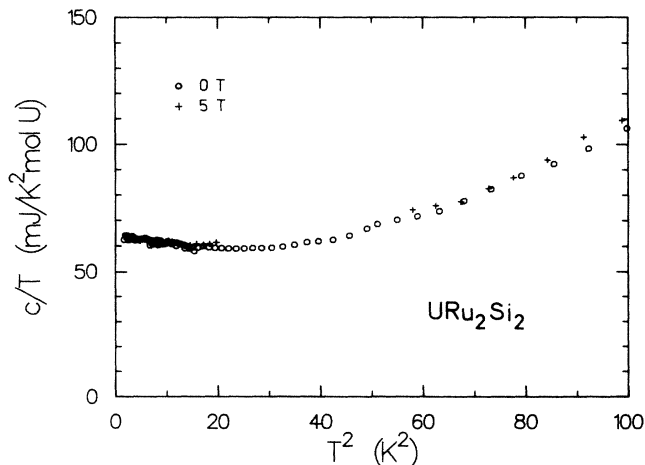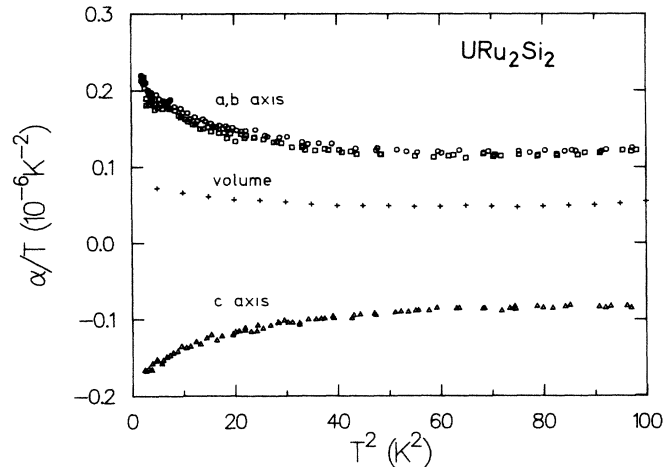

FIG. 6. The thermal expansion of URu$_2$Si$_2$ plotted as α_i/T vs T^2; α_a (○), α_b (□), α_c (△), α_v (+).

Γ_e of 25. Although this value is an order of magnitude larger than the free-electron value, it is substantially smaller than the corresponding value in the heavy-fermion systems UPt$_3$ (65), CeAl$_3$ (−200), etc. Further combining of the specific-heat and thermal-expansion data, we concentrate on the jumps in these two quantities at the phase transition. According to the Ehrenfest relation, the pressure dependence of the ordering temperature is related to Δc and $\Delta\alpha_v$ by $\partial\ln T_N/\partial p = 3\Delta\alpha_v V_m/\Delta c$. Inserting the above-quoted results we obtain a value of 8.0 Mbar^{-1} for the relative pressure dependence of T_N. A direct measurement of this pressure dependence in high-pressure resistivity studies[6] resulted in a value of 6.8 Mbar^{-1}, in satisfying agreement with the above-given value. The thermal-expansion anomalies at the phase transition are of the order of 5×10^{-6} K^{-1} and not particularly large. This does not point to a crystallographic nature of the phase transition at 17.5 K. Nevertheless, a close connection between magnetic or electronic properties, on the one hand, and the lattice parameters, on the other hand, can be inferred from the present data. In the specific-heat data reported by Schlabitz *et al.*, a curve is shown for the difference in specific heat Δc between URu$_2$Si$_2$ and ThRu$_2$Si$_2$.[1] Besides a peak at 17.5 K, Δc exhibits a broad maximum around 30 K that is attributed to a crystal-field effect. Around the same temperature a broad maximum is also observed in the volume thermal-expansion coefficient; see Fig. 2. This maximum can be discerned even without subtracting the phonon contribution to the thermal expansion, indicating that the relative strength of the crystal-field contribution to the thermal expansion exceeds that to the specific heat. The temperature dependence of the coefficient α_v, as represented by the data of Fig. 2, is weak compared to that of the specific heat, shown in Fig. 4. The crossing of the thermal-expansion coefficients along the different crystallographic directions as shown in Fig. 1, points to a complex temperature dependence of the c/a ratio. The temperature dependence of this parameter has some resemblance to that of the susceptibility along the tetragonal axis. A broad extremum around 60 K is present in the c/a ratio, as

FIG. 5. The specific heat of URu$_2$Si$_2$ plotted as c/T vs T^2 in zero field (○) and in an applied field of 5 T (+).

well as in the susceptibility.[2] This temperature of 60 K is close to the temperature where the resistivity exhibits a broad maximum, 75 K. This latter temperature is sometimes considered as the temperature below which coherent scattering of the conduction electrons occurs. This coherence apparently leads in this view to increased values of the c/a ratio in this particular compound. A more simple interpretation of the susceptibility data, including the maximum around 60 K and a qualitative description of the magnetization, however, can be found in a crystal-field calculation in which the system is described by a singlet ground state, a first singlet excited state at 40 K, a second one at 170 K, and a doublet at 550 K.[16] The broad anomalies in the specific-heat and thermal-expansion coefficient agree with this picture. Magnetic order at 17.5 K is compatible with this crystal-field calculation, although the values for the ordered magnetic moment largely exceed the results derived from neutron experiments.

[1]W. Schlabitz, J. Bauman, B. Politt, U. Rauchschwalbe, H. M. Mayer, U. Ahlheim, and C. D. Bredl, Z. Phys. B **62**, 171 (1986).

[2]T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. **55**, 2727 (1985).

[3]C. Broholm, J. K. Kjems, W. J. L. Buyers, T. T. M. Palstra, A. A. Menovsky, and J. A. Mydosh (unpublished).

[4]H. Ptasiewicz-Bak, J. Leciejewicz, and A. Zygmunt, J. Phys. F **11**, 1225 (1981).

[5]L. Chelmicki, J. Leciejewicz, and A. Zygmunt, J. Phys. Chem. Solids **46**, 529 (1985).

[6]F. R. de Boer, J. J. M. Franse, E. Louis, A. A. Menovsky, J. A. Mydosh, T. T. M. Palstra, U. Rauchschwalbe, W. Schlabitz, F. Steglich, and A. de Visser, Physica B **138**, 1 (1986).

[7]H. R. Ott, K. Andres, and P. H. Schmidt, Physica B **102**, 148 (1980).

[8]M. B. Maple, J. W. Chen, Y. Dalichaouch, T. Kohara, C. Rossel, M. S. Torikachvili, M. W. McElfresh, and J. D. Thompson, Phys. Rev. Lett. **56**, 185 (1986).

[9]N. H. Luong, J. J. M. Franse, and T. D. Hien, J. Magn. Magn. Mater. **50**, 153 (1985).

[10]C. F. Kamma, P. H. Frings, J. C. P. Klaasse, and J. J. M. Franse, Physica B **119**, 72 (1983).

[11]P. H. Frings and J. J. M. Franse, J. Magn. Magn. Mater. **51**, 141 (1985).

[12]A. de Visser, J. J. M. Franse, and A. Menovsky, J. Phys. F **15**, L53 (1985).

[13]D. Jaccard and J. Flouquet, J. Magn. Magn. Mater. **47-48**, 45 (1985).

[14]A. Menovsky and J. J. M. Franse, J. Cryst. Growth **65**, 286 (1983).

[15]E. Louis, A. de Visser, A. Menovsky, and J. J. M. Franse, Physica B **144**, 48 (1986).

[16]G. J. Nieuwenhuys (unpublished).