Invited paper

Magnetic phase transitions in heavy-fermion compounds studied by thermal-expansion measurements

A. de Visser, A. Lacerda a, J.J.M. Franse and J. Flouquet a

Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckeniersstraat 65, NL-1018 XE Amsterdam, The Netherlands

a Centre de Recherches sur les Très Basses Températures, CNRS, BP 166X, F-38042 Grenoble Cédex, France

On alloying the heavy-fermion compounds CeRu₂Si₂ and UPt₃ with small amounts of La and Pd, respectively, long-range antiferromagnetic order develops with Néel temperatures in the order of a few kelvin. In order to study the volume effects that are involved with the evolution into the long-range ordered state, we have performed thermal-expansion measurements on the pure and doped systems. The results are compared with data on antiferromagnetic URu₂Si₂. Subsequently, we discuss thermal-expansion measurements in high-magnetic fields, in particular on CeRu₂Si₂, where a metamagnetic-like transition occurs as the intersite-correlations collapse in a field of 7.8 T. Most of the measurements have been performed on single-crystalline samples, revealing a pronounced anisotropy.

I. Introduction

In the past few years it has been recognized that most of the heavy-fermion systems are close to an antiferromagnetic instability. For instance, in the systems CeRu₂Si₂ [1] and UPt₃ [2] long-range magnetic order develops for doping with small amounts of La and Pd, respectively. Furthermore, a metamagnetic-like transition is observed in the liquid helium temperature range for CeRu₂Si₂ [1] and UPt₃ [3] at 7.8 and 20 T, respectively. Although the origin of the long-range magnetic order is far from being settled, it is conceivable that alloying leads to an increase of the local character of the 4f or 5f electron states, depending on the degree of hybridization with the p or d-orbitals of the ligand atoms. The tendency towards localization on doping reduces the bonding and thus leads to an increase of the volume.

In previous work [4,5] we have investigated the volume effects that are related with the onset of the heavy-fermion behaviour in the compounds CeCu₆, CeRu₂Si₂, URu₂Si₂, UBe₁₃ and UPt₃. All these compounds show large positive coefficients of volume thermal expansion at low temperatures, implying a strong reduction of the volume as the f-electrons lose their local character and the formation of the heavy-fermion state sets in. Furthermore, anomalously large Grüneisen parameters are obtained: \( \Gamma_\text{hf} = V'_m a / \gamma \approx 100 \), where \( a \) and \( \gamma \) are the coefficients of the terms linear in temperature of the volume expansion and the specific heat, respectively, \( V'_m \) is the molar volume and \( \kappa \) is the compressibility. The large values for \( \Gamma_\text{hf} \) indicate a strong volume variation of the quasiparticle bands.

In this paper we aim to discuss some first results of a study of the volume effects that accompany long-range magnetic order in heavy-fermion compounds. We focus on (Ce, La)Ru₂Si₂, U(Pt, Pd)₃ and URu₂Si₂. Thermal expansion measurements have been performed using a sensitive capacitance dilatometer [6] with a detection limit \( \Delta L / L \approx 10^{-8} \). The data have mostly been taken on single-crystalline samples (dimensions 2–5 mm) allowing for an investigation of anisotropy effects. As it will appear, large anomalies are observed at the ordering temperatures, indicating that thermal expansion is a powerful technique to study the evolution of the ordered state.

2. \((\text{Ce, La})\text{Ru}_2\text{Si}_2\)

The \(\text{Ce}_{1-x}\text{La}_x\text{Ru}_2\text{Si}_2\) compounds crystallize in the tetragonal structure. In fig. 1 we show the coefficient of

![Fig. 1. Coefficient of volume expansion of single-crystalline Ce₁₋ₓLaₓRu₂Si₂ for \( x = 0.00 \) (○), \( x = 0.05 \) (●) and \( x = 0.20 \) (+).](image-url)
volume expansion ($\alpha_v$) for $x = 0.00$, 0.05 and 0.20, in the temperature interval $1.5 \, K < T < 30 \, K$. For pure CeRu$_2$Si$_2$ we reported [7] two pronounced anomalies: (i) a huge low-temperature peak centered at $T_m = 9 \, K$, that is attributed to the onset of antiferromagnetic intersite correlations, and (ii) a negative crystal-field contribution with a minimum at 120 K, yielding a first doublet-doublet splitting of 288 K. In the 5% La compound $T_m$ is shifted to 6 K [8]. Combining the $\alpha_v(T)$ measurements with specific heat data $c(T)$ [1,9], we obtain low-temperature Grüneisen parameters $\Gamma_{\text{eff}}(T \rightarrow 0) = \Gamma_{\text{eff}}$ of 160 and 220 for $x = 0.00$ and 0.05, respectively. The increase of $\Gamma_{\text{eff}}$ with La contents is related to the approach of the magnetic instability. In a plot in reduced units, $\Gamma_{\text{eff}}(T)/\Gamma(T_m)$ versus $T/T_m$, the curves for $x = 0.00$ and 0.05 coincide (see ref. [8]). Thus the two compounds have the same behaviour on normalized energy scales.

Long-range magnetic order occurs for La concentrations above 7% [10]. The ordering vector is incommensurate ($k = (0.309,0,0)$). For the 20% La compound the Neél temperature ($T_N$) equals 5.9 K and the ordered moment amounts to 1.2$\mu_B$/Ce-atom. In fig. 2 we show its coefficient of linear thermal expansion along ($\alpha_\parallel$) and at right angles ($\alpha_\perp$) to the tetragonal (c) axis. The expansion is rather isotropic ($\alpha_\parallel \approx \alpha_\perp$) as was also observed for $x = 0.00$ [7] and 0.05 [8]. The decrease of $\alpha_\parallel$ above $T_N$ with increasing temperature is related with the loss of antiferromagnetic spin-fluctuation phenomena. The magnetic order is observed as a sharp drop of $v_{\parallel}$ and $v_{\perp}$, with a quasi-linear behaviour below $T_N$. A second magnetic transition [30] of similar shape is observed at $T_{N_2} = 2.0 \, K$. In neutron-scattering experiments [10] the second transition can hardly be discerned (it turns up only in the third order harmonic). Applying the Ehrenfest relation $dT_N/dP = T_N\alpha_N/\alpha_v$, where $\Delta N$ and $\Delta \alpha$ are the jumps in the coefficient of volume expansion and specific heat at $T_N$, respectively, and $V_m = 5.2 \times 10^{-5}$ m$^3$/mol, we derive a depression of $T_1 = T_N$ and $T_{N_2}$ with pressure. Using the values for $\Delta \alpha$ of $-1.9$ and $-0.2$ $J$/Kmol [11] and data for $\Delta N$, deduced from fig. 2, we calculate $dT_N/dP = -0.56$ K/kbar and $dT_{N_2}/dP = -0.70$ K/kbar, respectively.

In fig. 3, we show the field derivative of the magnetostriction, $L^{-1}(dL/dB)$, with $(dL/L)||B||c$ (i.e. the easy axis for magnetization [12]) at a temperature of 1.3 K, for $x = 0.00$, 0.05 and 0.20. The metamagnetic transition turns up as a sharp peak at 7.8 T in pure CeRu$_2$Si$_2$, whereas in the 5% La compound the peak is shifted downwards to 5.7 T and has become much broader. In the 20% La compound two sharp transitions occur at 1 and 3.2 T, related to the phase boundaries of $T_{N_1}$ and $T_{N_2}$. Above 3.2 T a shoulder appears, indicating that magnetic fluctuations are still present in the field induced paramagnetic phase. Similar anomalies have been observed in the differential susceptibility [13].

We have also studied the low-temperature anomaly in $\alpha_v(T)$ for CeRu$_2$Si$_2$ as function of an external field along the c-axis [14]. In a magnetic field the anomaly in $\alpha_v$ rapidly shifts towards lower temperatures, where it becomes very sharp and, surprisingly, changes sign at the metamagnetic transition ($B^* = 7.8$ T) (see fig. 4). The field dependence of $T_N$ is shown in the inset of fig. 4. $T_m(B)$ mimics qualitatively the boundary of a crossover phase diagram separating a highly correlated antiferromagnetic low temperature phase and a polarized paramagnetic phase. Having recently extended our measurements down to lower temperatures, we have ob-

Fig. 2. Coefficient of linear thermal expansion along (o) and perpendicular (*) to the tetragonal axis for Ce$_{0.80}$La$_{0.20}$Ru$_2$Si$_2$. The solid line represents $\alpha_v/3$. Fig. 3. Magnetostriiction along the tetragonal axis (B||c) at $T = 1.3 \, K$ for Ce$_{1-x}$La$_x$Ru$_2$Si$_2$ for $x = 0.00$ (o), $x = 0.05$ (*) and $x = 0.20$ (+).
served that $B^*$ shifts down to 7.665 T and that for fields very close to $B^*$ $T_m$ decreases to approximately 300 mK [11]. In order to investigate further the nature of the transition for $T \to 0$, more experiments are in progress. Using a scaling ansatz and elementary thermodynamics, the data for $\alpha_\gamma(B)$ can be used to calculate $\gamma(B)$. It was found that $\gamma$ exhibits a maximum at $B^*$. For a discussion of the scaling ansatz we refer to ref. [14] and references therein. Similar $\alpha_\gamma(B)$ data have been obtained for the 5% La compound and are reported elsewhere [15].

3. $\text{U(Pt}_x\text{Pd}_{1-x})_3$

The $\text{U(Pt}_{1-x}\text{Pd}_{x})_3$ compounds crystallize in a hexagonal structure. The low-temperature properties of $\text{UPt}_3$ ($\gamma = 420$ mJ/molK$^2$) are governed by pronounced spin-fluctuation phenomena [16]. Superconductivity sets in at 0.5 K. The coefficient of thermal expansion of $\text{UPt}_3$ [17] is strongly anisotropic: positive in the basal plane ($\alpha_\parallel$) and negative (up to 40 K) with a minimum at 15 K along the hexagonal axis ($\alpha_\perp$). The volume expansion exhibits an anomaly at 10 K (fig. 5), that is attributed to the presence of antiferromagnetic correlations. On alloying $\text{UPt}_3$ with Pd, long-range magnetic order occurs in the concentration range between 1 and 10% Pd, with a maximum $T_N$ of 5.8 K for the 5% Pd compound [2]. The magnetic moments are directed along the $b$-axis [18]. The ordered moment is rather large, 0.6$\mu_B$/U-atom for $x = 0.05$, in contrast to the value of 0.02$\mu_B$/U-atom, that has been reported [19] for the long-range antiferromagnetic order found in some of the $\text{UPt}_3$ samples below 5 K. In the 5% Pd sample $T_N$ turns up as a large positive peak for $\alpha_\parallel$ and an even larger negative peak for $\alpha_\perp$ [20,21]. In the resulting volume expansion $T_N$ appears as a negative peak on the large heavy-fermion background (fig. 5). For comparison we have plotted in fig. 5 $\alpha_\gamma(T)$ for polycrystalline $\text{U(Pt}_{0.98}\text{Pd}_{0.02})_3$ [22] that orders at 3.3 K. However, as discussed elsewhere [16], preferred directions in our polycrystalline samples might lead to values for $\alpha_\gamma$ that do not represent the real volume effect, and thus some care should be taken when performing a quantitative analysis. Taking values for $\Delta c$ of $-1.45$ and $-0.24$ J/Kmol and for $\Delta \alpha_\gamma$ of $10 \times 10^{-6}$ and $9.6 \times 10^{-6}$ K$^{-1}$, the pressure dependence of $T_N$ amounts to $-0.17$ and $-0.56$ K/kbar, for $x = 0.05$ and 0.02, respectively. However, from resistivity measurements under pressure ($P_{\text{max}} = 4.4$ kbar) a value for $dT_N/dP$ of $-0.32$ K/kbar has been deduced for the 5% Pd compound [23]. Hence the initial pressure dependence as derived via the Ehrenfest relation is much weaker. For the 7% Pd compound the $T_N$ ($= 5.5$ K) is almost pressure independent [20]. Apparently, the rate of depression of $T_N$ decreases drastically with increasing Pd contents.

In an attempt to separate the heavy-fermion and the antiferromagnetic contribution to the thermal properties an analysis employing Grüneisen parameters has been made. For the 5% Pd sample the resulting Grüneisen parameters for the heavy-fermion and antiferromagnetic contributions amount to 73 and $-41$, respectively. The detailed analysis can be found in ref. [21].

4. $\text{URu}_2\text{Si}_2$

The tetragonal antiferromagnetic superconductor $\text{URu}_2\text{Si}_2$ has a Néel temperature $T_N = 17.5$ K [24]. Superconductivity sets in below 1.1 K. Although in this case a large anomaly has been observed in the specific heat at $T_N$, the ordered moment (directed along the c-axis) as observed by neutron-diffraction experiments [25] is small (0.02$\mu_B$/U-atom). The thermal expansion of single-crystalline $\text{URu}_2\text{Si}_2$ [26] is shown in fig. 6 for

![Fig. 5. Coefficient of volume expansion of single-crystalline $\text{U(Pt}_{1-x}\text{Pd}_x)_3$ for $x = 0.00$ (o) and $x = 0.05$ (o), and for a polycrystalline sample with $x = 0.02$.](image)
The quasi-linear behaviour of Ce$_{0.80}$La$_{0.20}$Ru$_2$Si$_2$ suggests a non-gap-like behaviour, of order as that of a spin or charge density wave [28]. Opening of a gap over a part of the Fermi surface in both U(Pt$_{0.9}$Pd$_{0.1}$) and URu$_2$Si$_2$, classifying the type anomalies in the specific heat and latter compound. On the other hand, the shape of the by crystal-field effects and is probably intimately re­

lated to these.

The anomalies observed at the Neél temperature for La doped CeRu$_2$Si$_2$ and Pd doped UPt$_3$ yield a strong increase of the volume as the magnetic order sets in. Accordingly, $T_N$ is depressed with pressure, as follows from the analysis using the Ehrenfest relation. This behaviour contrasts with the volume effect of URu$_2$Si$_2$ at $T_N$, that has the opposite sign. This strongly suggests that different mechanisms are at the origin of the long­

range ordered state, as might also be expected from the very different size of the ordered moments. The long­

range magnetic order in the doped systems develops out of a strongly correlated electron state, whereas the mag­

netism in URu$_2$Si$_2$ evolves from a state that is governed by crystal-field effects and is probably intimately re­

lated to these. It is, therefore, of interest to investigate the pressure dependence of the crystal-field levels in the latter compound. On the other hand, the shape of the anomaly at $T_N$ in the resistivity, and the exponential-like anomalies in the specific heat and $\alpha_v(T)$, evidence the opening of a gap over a part of the Fermi surface in both U(Pt$_{0.95}$Pd$_{0.05}$)$_3$ and URu$_2$Si$_2$, classifying the type of order as that of a spin or charge density wave [28]. The quasi-linear behaviour of $\alpha_v(T)$ below $T_N$ of Ce$_{0.80}$La$_{0.20}$Ru$_2$Si$_2$ suggests a non-gap-like behaviour, which is probably related to the incommensurate ordering vector.

To summarize, we have presented a first study of the volume effects at the magnetic phase transitions in heavy-fermion systems. If the magnetic order develops out of a strongly correlated electron system, a strong reduction of the coefficient of volume expansion is observed (the same conclusion holds for the transition to the superconducting state in UPt$_3$, URu$_2$Si$_2$ and UBe$_{13}$ [29]). Heavy-fermion behaviour persists in the ordered state (in particular in the U(Pt, Pd) system), which makes it difficult to separate out the contribution of the long-range order. Thermal-expansion measurements in an applied magnetic field on CeRu$_2$Si$_2$ show huge effects at the metamagnetic transition. In conclusion, thermal expansion appears to be a powerful tech­

nique in the investigation of the approach of the mags­

netic instability in the heavy-fermions systems.

The research of A.d.V. was made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences. A.L. is supported by Conselho Nacional de Desenvolvimento Cientifico e Technologico (CNPq).

References

Flouquet, J. Voirom and F.J. Ohkawa, Phys. Rev. B 40
408.
[19] G. Aeppli, E. Bücher, C. Broholm, J.K. Kjems, J. Baum-
499.
B 161 (1989) 337.
Dirkmaat, P.H. Kes, G.J. Nieuwenhuys and J.A Mydosh,
T.T.M. Palsstra, A.A. Menovsky and J.A. Mydosh, Phys.
[26] A. de Visser, F.E. Kayzel, A.A. Menovsky, J.J.M. Franse,
J. van den Berg and G.J. Nieuwenhuys, Phys. Rev. B 34
(1986) 8168.
[27] F.R. de Boer, J.J.M. Franse, E. Louis, A.A. Menovsky,
J.A. Mydosh, T.T.M. Palsstra, U. Rauchschwalbe, W.
Schlabitz, F. Steglich and A. de Visser, Physica B 138
(1986) 1.
[29] A. de Visser, F.E. Kayzel, A.A. Menovsky, J.J.M. Franse,
K. Hasselbach, A. Lacerda, L. Taillefer, J. Flouquet and