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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, Valckenierstraat 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 $CeRu_2Si_2$ and UPt_3 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 URu_2Si_2. Subsequently, we discuss thermal-expansion measurements in high-magnetic fields, in particular on $CeRu_2Si_2$, 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.

1. 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 $CeRu_2Si_2$ [1] and UPt_3 [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 $CeRu_2Si_2$ [1] and UPt_3 [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 $CeCu_6$, $CeRu_2Si_2$, URu_2Si_2, UBe_{13} and UPt_3. 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: $\Gamma_{hf} = V_m a/\kappa\gamma \approx 100$, where a and γ 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 κ is the compressibility. The large values for Γ_{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)Ru_2Si_2, U(Pt, Pd)$_3$ and URu_2Si_2. 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. (Ce, La)Ru_2Si_2

The $Ce_{1-x}La_xRu_2Si_2$ compounds crystallize in the tetragonal structure. In fig. 1 we show the coefficient of

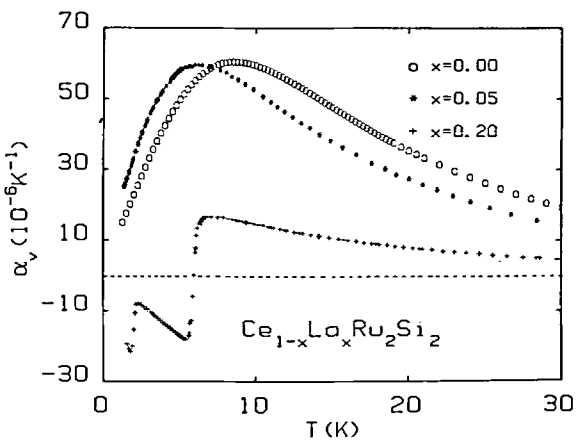

Fig. 1. Coefficient of volume expansion of single-crystalline $Ce_{1-x}La_xRu_2Si_2$ for $x = 0.00$ (○), $x = 0.05$ (*) and $x = 0.20$ (+).

volume expansion (α_v) for $x = 0.00$, 0.05 and 0.20, in the temperature interval 1.5 K $< T <$ 30 K. For pure $CeRu_2Si_2$ 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 $\Gamma_{eff}(T \rightarrow 0) = \Gamma_{hf}$ of 160 and 220 for $x = 0.00$ and 0.05, respectively. The increase of Γ_{hf} with La contents is related to the approach of the magnetic instability. In a plot in reduced units, $\Gamma_{eff}(T)/\Gamma(T_m)$ 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 ($\vec{k} = (0.309,0,0)$). For the 20% La compound the Néel 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 ($\alpha_\parallel \propto \alpha_\perp$) as was also observed for $x = 0.00$ [7] and 0.05 [8]. The decrease of α_v 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 $\alpha_\parallel$ and $\alpha_\perp$, with a quasi-linear behaviour below T_N. A second magnetic transition [30] of similar shape is observed at $T_{N2} = 2.0$ K. In neutron-scattering experiments [10] the second transition can hardly be discerned

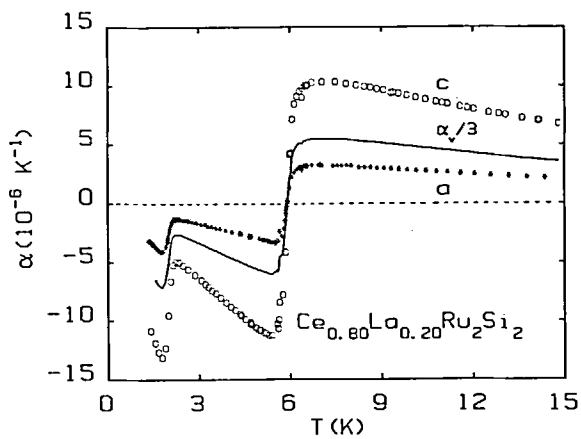

Fig. 2. Coefficient of linear thermal expansion along (○) and perpendicular (*) to the tetragonal axis for $Ce_{0.80}La_{0.20}Ru_2Si_2$. The solid line represents $\alpha_v/3$.

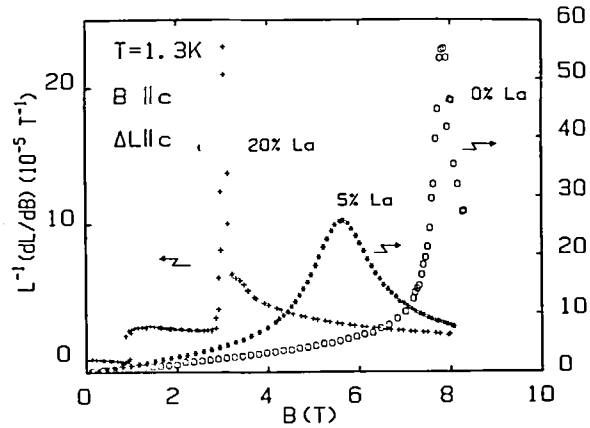

Fig. 3. Magnetostriction along the tetragonal axis ($B \| c$) at $T = 1.3$ K for $Ce_{1-x}La_xRu_2Si_2$ for $x = 0.00$ (○), $x = 0.05$ (*) and $x = 0.20$ (+).

(it turns up only in the third order harmonic). Applying the Ehrenfest relation $dT_N/dP = T_N V_m \Delta\alpha_v/\Delta c$, where $\Delta\alpha_v$ and Δc 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 $T_{N1} \equiv T_N$ and T_{N2} with pressure. Using the values for Δc of -1.9 and -0.2 J/Kmol [11] and data for $\Delta\alpha_v$ deduced from fig. 2, we calculate $dT_{N1}/dP = -0.56$ K/kbar and $dT_{N2}/dP = -0.70$ 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 $CeRu_2Si_2$, 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_{N1}, and T_{N2}. 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 $CeRu_2Si_2$ as function of an external field along the c-axis [14]. In a magnetic field the anomaly in α_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_m is shown in the inset of fig. 4. $T_m(B)$ mimics qualitatively the boundary of a cross-over 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-

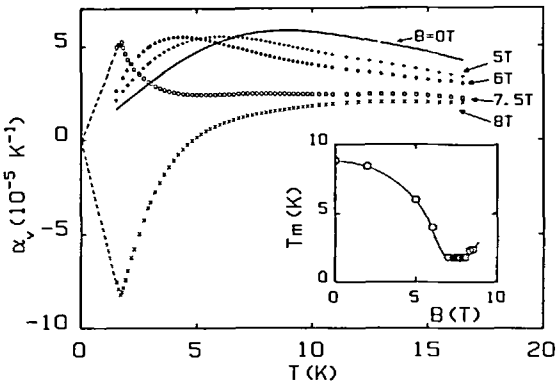

Fig. 4. Coefficient of volume expansion of $CeRu_2Si_2$ for magnetic fields as indicated. The inset shows the field dependence of the extremal temperature T_m (after ref. [14]).

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 $\alpha_v(B)$ can be used to calculate $\gamma(B)$. It was found that γ exhibits a maximum at B^*. For a discussion of the scaling ansatz we refer to ref. [14] and references therein. Similar $\alpha_v(B)$ data have been obtained for the 5% La compound and are reported elsewhere [15].

3. U(Pt, Pd)$_3$

The $U(Pt_{1-x}Pd_x)_3$ compounds crystallize in a hexagonal structure. The low-temperature properties of 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 UPt_3 [17] is strongly anisotropic: positive in the basal plane ($\alpha_\perp$) and negative (up to 40 K) with a minimum at 15 K along the hexagonal axis ($\alpha_\parallel$). The volume expansion exhibits an anomaly at 10 K (fig. 5), that is attributed to the presence of antiferromagnetic correlations. On alloying 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 UPt_3 samples below 5 K. In the 5% Pd sample T_N turns up as a large positive peak for $\alpha_\perp$ and an even larger negative peak for $\alpha_\parallel$ [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 $\alpha_v(T)$ for polycrystalline $U(Pt_{0.98}Pd_{0.02})_3$ [22] that orders at 3.3 K. However, as discussed elsewhere [16], preferred directions in our polycrystalline samples might lead to values for α_v that do not represent the real volume effect, and thus some care should be taken when performing a quantitative analysis. Taking values for Δc of -1.45 and -0.24 J/Kmol and for $\Delta\alpha_v$ of 10×10^{-6} and 9.6×10^{-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 ($P_{max} = 4.4$ 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. URu_2Si_2

The tetragonal antiferromagnetic superconductor URu_2Si_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 URu_2Si_2 [26] is shown in fig. 6 for

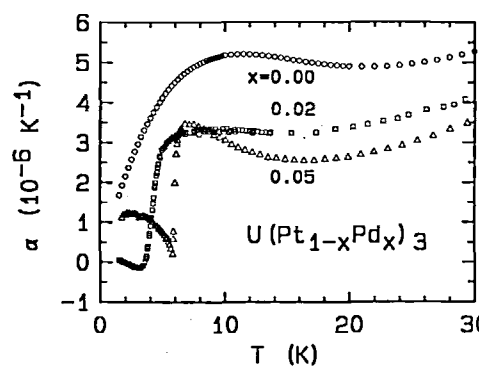

Fig. 5. Coefficient of volume expansion of single-crystalline $U(Pt_{1-x}Pd_x)_3$ for $x = 0.00$ (○) and $x = 0.05$ (△), and for a polycrystalline sample with $x = 0.02$.

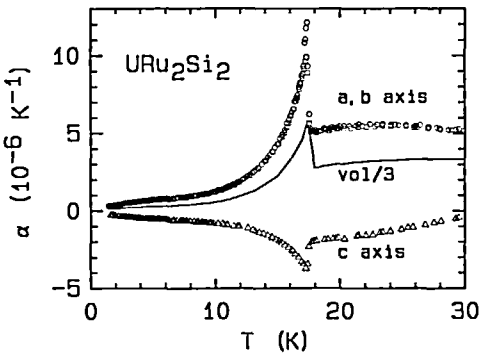

Fig. 6. Coefficient of linear thermal expansion of URu_2Si_2 along the a (○), b (□) and c (△) axis (after ref. [26]). The solid line represents $\alpha_v/3$.

1.5 K $< T <$ 30 K, where α is strongly anisotropic. Three anomalies are observed: (i) a broad low-temperature contribution near 5 K, leading to a heavy-fermion Grüneisen parameter of 25, (ii) a sharp peak at T_N, and (iii) a crystal field contribution centered at 25 K. The latter is tentatively ascribed to a singlet-singlet splitting of 40 K. Employing the Ehrenfest relation it is found that T_N increases with pressure at a rate of 0.14 K/kbar, in good agreement with a value of 0.12 K/kbar that followed from a high-pressure resistivity study [27].

5. Concluding remarks

The anomalies observed at the Néel temperature for La doped $CeRu_2Si_2$ 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_2Si_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 magnetism in URu_2Si_2 evolves from a state that is governed by crystal-field effects and is probably intimately related 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_2Si_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 $Ce_{0.80}La_{0.20}Ru_2Si_2$ 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_2Si_2 and UBe_{13} [29]). Heavy-fermion behaviour persists in the ordered state (in particular in the $U(Pt, Pd)_3$ system), which makes it difficult to separate out the contribution of the long-range order. Thermal-expansion measurements in an applied magnetic field on $CeRu_2Si_2$ show huge effects at the metamagnetic transition. In conclusion, thermal expansion appears to be a powerful technique in the investigation of the approach of the magnetic instability in the heavy-fermions systems.

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