Thermal properties of heavy-fermion $CeRu_2Si_2$

A. Lacerda, A. de Visser,* P. Haen, P. Lejay, and J. Flouquet
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique, Boîte Postale 166 X, 38042 Grenoble CEDEX, France
(Received 30 May 1989)

We present measurements of the coefficients of linear thermal expansion of single-crystalline samples of the tetragonal heavy-fermion compound $CeRu_2Si_2$, and its nonmagnetic analog $LaRu_2Si_2$, in the temperature range 1.5–270 K. The electronic part of the thermal expansion of $CeRu_2Si_2$ yields two distinct anomalies: (1) a huge positive contribution, caused by the (antiferro)magnetic interactions between the quasiparticles, centered at 9 K, and (2) a negative crystal-field contribution centered at 120 K. The data are compared with existing specific-heat data ($T < 100$ K). An analysis in terms of Grüneisen parameters yields the very large value of $\Gamma_{hf} = 190$ for the low-temperature contribution and a value $\Gamma_{cf} = -5.3$ for the crystal-field contribution. A quantitative analysis using a simple single resonance-level model yields a Kondo-type temperature of 19 K. An analysis of the crystal-field contribution yields a first excited level at 288 K. We also discuss low-temperature scaling behavior by comparing new magnetostriction measurements, that cover the metamagnetic behavior, with magnetization data.

I. INTRODUCTION

Among the rare-earth ternaries with the tetragonal $ThCr_2Si_2$ structure, the compound $CeRu_2Si_2$ attracts much attention due to its heavy-fermion properties and the related metamagneticlike transition. Evidence for the presence of a strongly interacting electron system at low temperatures has mainly been deduced from specific-heat measurements,[1–4] yielding a coefficient of the linear electronic term $\gamma \cong 350$ mJ/mol K^2, which allows a Fermi-liquid description with a large value for the effective mass of the quasiparticles. Consistent with this, low-temperature susceptibility (χ) measurements[5,6] on polycrystalline samples show a Pauli-like χ of (150–200) $\times 10^{-9}$ m^3/mol. The ratio of the measured susceptibility and the susceptibility calculated from the measured γ value (χ_c), $R = \chi/\chi_c = 5.8 \times 10^6 (\chi/\gamma)$ [with χ and γ in Système International (SI) units] amounts to 2.5–3.5 (for $T \to 0$). According to the phenomenological trends for narrow-band metals as formulated by DeLong,[7] the deduced value for R indicates that $CeRu_2Si_2$ has a (para)magnetic ground state, and, in fact, no superconductivity (or long-range magnetic order) has been observed in this compound down to 20 mK.[5,6,8]

Specific-heat measurements over a large temperature range ($1.5 < T < 100$ K) were performed by Besnus *et al.* (Ref. 1). After subtracting the lattice contribution, deduced from measurements on isostructural $LaRu_2Si_2$, two distinct anomalies were found at 11 and 84 K. From their analysis the authors concluded that the Ce atoms in $CeRu_2Si_2$ are in a doublet crystal-field ground state, the $2J+1$ Ce levels being split into three doublets. The Kondo effect on the doublet ground state gives rise to the low-temperature anomaly at 11 K, which in the single-ion Kondo $S = \frac{1}{2}$ model leads to a Kondo temperature $T_K = 24$ K. The second anomaly (at 84 K) has been interpreted as a Schottky anomaly, caused by the population of the first-excited crystal-field doublet, lying 220 K above the ground-state doublet.

Low-field susceptibility measurements[8] ($T < 300$ K) on single-crystalline samples reveal that the magnetic parameters are strongly anisotropic with the tetragonal axis (c axis) as the easy axis for magnetization: $\chi_\parallel/\chi_\perp = 15$ at 10 K. Below 70 K, $\chi_\parallel$ yields an increasing departure from the Curie-Weiss law and a weak maximum at 10 K; both have been attributed to the presence of antiferromagnetic interactions. The considerable deviation from the Curie-Weiss law below 200 K for $\chi_\perp$ has been ascribed to the crystal field.

As function of an external magnetic field a metamagneticlike transition is observed[1,8,9] at $H^* = 8$ T, for a field direction along the c axis. Studies of the temperature dependence of H^* by means of magnetization and magnetoresistivity[8] indicate that this transition is observed up to ~ 15 and 70 K, respectively. These high-field data can be connected with the disappearance of magnetic correlations, notably a collapse of the antiferromagnetic interactions between the quasiparticles above H^*. Strong support for such an interpretation comes from inelastic neutron scattering experiments.[10,11]

The magnetic properties of $CeRu_2Si_2$ bear close similarities with the ones of the heavy-fermion superconductor UPt_3 (Ref. 12). For this compound a maximum in $\chi(T)$ is observed at 17 K and a metamagneticlike transition at 20 T. Both phenomena are only observed for a field direction in the hexagonal plane, indicating a two-dimensional character, in contrast to the one-dimensional behavior of $CeRu_2Si_2$. Furthermore, alloying studies, e.g., $(Ce,La)Ru_2Si_2$ (Ref. 1) and $U(Pt,Pd)_3$ (Ref. 13), reveal the appearance of long-range antiferromagnetic order for relatively small amounts of the doped elements. Apparently, both compounds are close to an antiferromag-

netic instability.

In a recent paper[14] it has been demonstrated that measurements of the coefficients of thermal expansion of heavy-fermion systems are of great interest as the volume effects related with the formation of the quasiparticle bands are large ($\Delta V/V \sim 10^{-4}$). The volume effects are usually described employing a phenomenological Grüneisen parameter, Γ, that represents the coupling between the heavy electrons and the lattice. The temperature dependence of Γ gives important information about the relevant energy scales. The underlying mechanism for the energy scales might be found in the single-ion Kondo or Kondo-lattice effect and the onset of strong (anti)ferromagnetic spin fluctuations, eventual in the presence of (and thus in a possible admixture with) crystalline electric field effects.

In view of the aforementioned unusual thermal and magnetic properties, it is of interest to investigate how these influence the lattice parameters and thus the volume. In this paper we present thermal-expansion measurements on a single-crystalline sample of $CeRu_2Si_2$, and its nonmagnetic analog $LaRu_2Si_2$, over a wide temperature range: $1.5 < T < 270$ K. The results are compared with specific-heat measurements[1] ($T < 100$ K), which allows us to perform an analysis in terms of Grüneisen parameters. We then analyze the high-temperature part of the data in a crystal-field model. In a first attempt to model the low-temperature contribution we make use of a simple resonance-level model. Previous thermal-expansion measurements[15] were performed only below 100 K. The wide temperature range investigated in the present experiments allows, however, for a more extended analysis.

We also present a complete set of low-temperature magnetostriction measurements on a single-crystalline sample in the field region that covers the metamagnetic-like transition. These data (with absolute values in contrast to earlier results[9]) will be compared with magnetization data exploring a simple scaling law[9] for the volume dependence of the magnetization.

II. EXPERIMENT

$CeRu_2Si_2$ and $LaRu_2Si_2$ crystallize in the $ThCr_2Si_2$ structure.[16] The lattice parameters are given by $a = 4.192$ Å and $c = 9.78$ Å in the Ce case, and by $a = 4.215$ Å and $c = 9.93$ Å in the La case. With two formula units per unit cell, the molar volume (V_m) amounts to 5.17×10^{-5} and 5.31×10^{-5} m^3/mol, respectively.

Single-crystalline samples of $CeRu_2Si_2$ and $LaRu_2Si_2$ were grown by the Czochralski technique. As starting materials served high-purity elements Ce (99.99%), Si (>99.999%), and La (99.99%), supplied by Johnson-Matthey, and Ru (99.999%) supplied by Leico Ind. Inc. The as-grown samples were machined by means of spark erosion into the proper shape, i.e., in this particular case, a parallelepiped (edge ~3 mm), with flat and planparallel surfaces containing the crystallographic axes. On both samples measurements have been performed along ($\alpha_\parallel$) and perpendicular ($\alpha_\perp$) to the tetragonal axis. In the case of $CeRu_2Si_2$ $\alpha_\perp$ was taken along the [100] direction. Measurements of the coefficient of linear thermal expansion, $\alpha = 1/L\,(dL/dT)$, were performed using a sensitive three-terminal capacitance method. The samples were mounted in a parallel-plate capacitance cell, machined out of oxygen-free high-conductivity copper.[17] Data points were taken stepwise. The accuracy decreases with increasing temperature due to thermal gradients over the cell, and amounts to 5×10^{-7} K^{-1} at 270 K. Below 50 K temperatures were read with a carbon-glass thermometer and those above with a platinum resistor. The coefficient of linear magnetostriction, $\lambda' = 1/L\,(dL/dB)$, was measured by placing the capacitance cell in a superconducting solenoid with a field limit of 8.5 T. By rotating the cell the magnetostriction could be measured parallel and at right angles to the field. Measurements have been performed at 4.2 and 1.3 K.

III. RESULTS

The coefficients of linear thermal expansion $\alpha_\parallel$ and $\alpha_\perp$, for single-crystalline $CeRu_2Si_2$ and its non-f-electron counterpart $LaRu_2Si_2$ are shown in Fig. 1(a). Apparent-

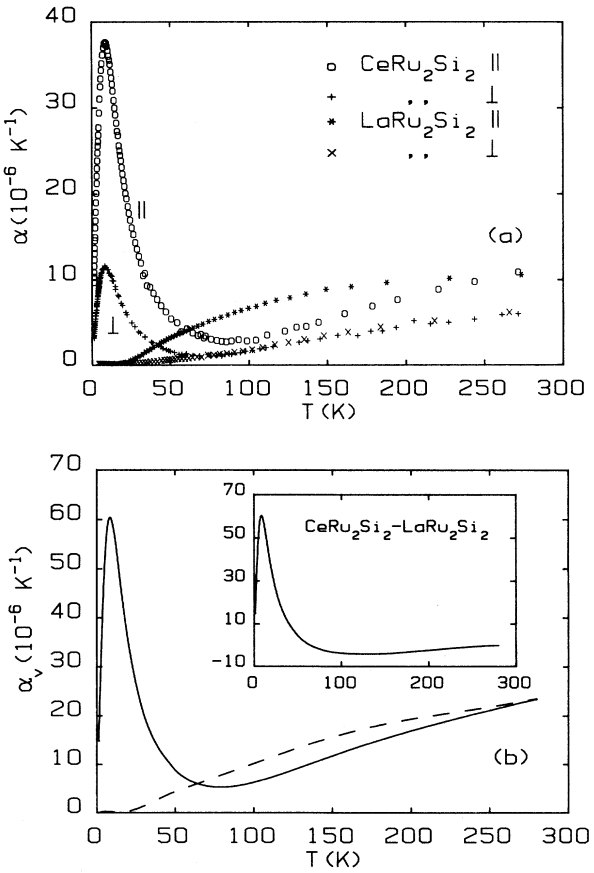

FIG. 1. (a) Coefficients of linear thermal expansion of $CeRu_2Si_2$ and $LaRu_2Si_2$ along (○ and *) and perpendicular (+ and ×) to the tetragonal axis, and (b) coefficients of volume thermal expansion of $CeRu_2Si_2$ (solid line) and $LaRu_2Si_2$ (dashed line). The inset shows the f-electron contribution to α_V of $CeRu_2Si_2$.

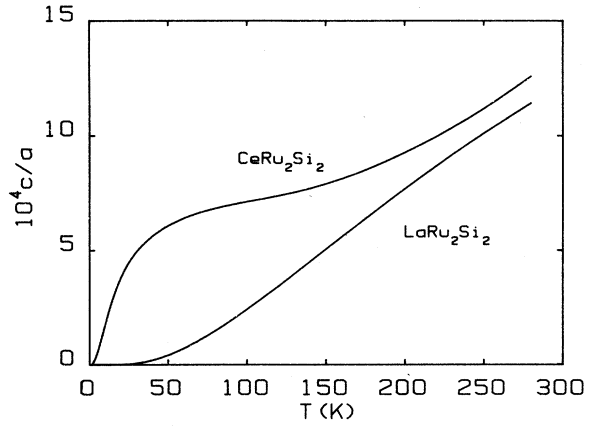

FIG. 2. The c/a ratio normalized to 0 at 1.5 K for $CeRu_2Si_2$ and $LaRu_2Si_2$.

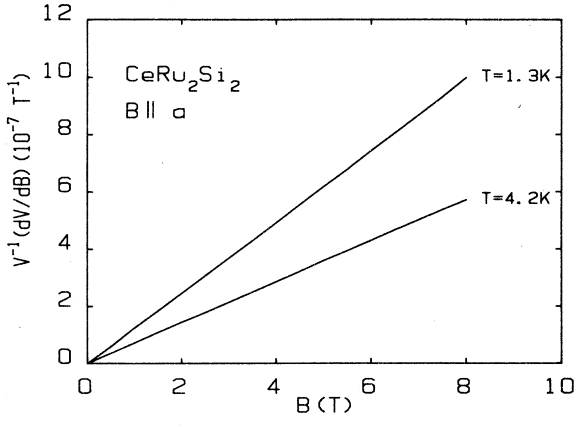

FIG. 4. Coefficient of volume magnetostriction for $CeRu_2Si_2$ ($B \| a$) at the temperatures indicated.

ly, when raising the temperature, the unit cell of $CeRu_2Si_2$ (and $LaRu_2Si_2$) expands over the whole temperature range, with a coefficient of expansion along the c axis larger than the one along the a axis. The volume expansion is calculated from $\alpha_V = 2\alpha_\perp + \alpha_\parallel$, after smoothing the data for $\alpha_\parallel$ and $\alpha_\perp$ with polynomial fits in selected temperature intervals. Results for α_V are shown in a separate figure [Fig. 1(b)] for the sake of clearness. The inset in Fig. 1(b) shows the excess thermal expansion of $CeRu_2Si_2$, $\Delta\alpha_V = 3\alpha_{el}$ obtained after subtracting the matrix $LaRu_2Si_2$. α_{el} becomes negative above ~ 65 K. The data in Fig. 1 are in good agreement with earlier measurements[15] ($T < 100$ K), that were performed on the same samples with a similar thermal expansion cell, except for the curve of $\alpha_\parallel$ for $CeRu_2Si_2$. In the previous experiment the low-temperature values of $\alpha_\parallel$ were about 25% smaller. The origin of the discrepancy between the two data sets is not clear yet, but possibly arises from repeated thermal cycling or aging effects of the unannealed sample. In Fig. 2 we show the change of c/a with respect to 1.5 K.

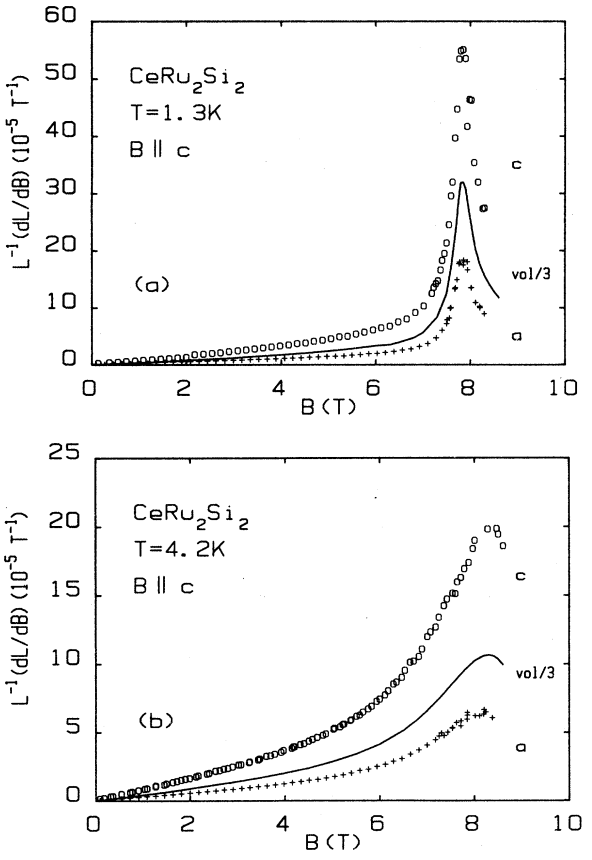

FIG. 3. Coefficients of linear magnetostriction for $CeRu_2Si_2$ ($B \| c$) along the c axis (○) and a axis (+), and $\lambda'_V/3$ (a) at 1.3 K and (b) at 4.2 K.

The coefficients of linear magnetostriction of $CeRu_2Si_2$ for a field direction along the c axis at 4.2 and 1.3 K are shown in Figs. 3(a) and 3(b), respectively. At both temperatures, measurements have been performed parallel $\lambda'_\parallel$ and at right angles of the field $\lambda'_\perp$. From Fig. 3 it follows that $\lambda'_\parallel$ is almost proportional to $\lambda'_\perp$ and that $\lambda'_\parallel \gg \lambda'_\perp$. The metamagneticlike transition is observed as a peak at 8.2 and 7.9 T at 4.2 and 1.3 K, respectively. Note that with decreasing temperature, the peak rapidly narrows and increases in height. Data for $B \| a$, for which direction no metamagneticlike transition occurs, are shown in Fig. 4. The coefficient of volume magnetostriction is in this case at least three orders of magnitude smaller.

IV. ANALYSIS

The f-electron contribution to the thermal expansion of $CeRu_2Si_2$, α_{el} [see inset Fig. 1(b)], exhibits two distinct anomalies. At low temperatures a large positive anomaly is present, centered at 9 K, but with a long tail towards higher temperatures. Since the low-temperature maxima in $c(T)$ and $\chi(T)$ are found at 11 and 10 K, respectively, these anomalies are likely to be attributed to the same physical phenomenon. We believe that this anomaly is due to the presence of magnetic correlations, in particular, a competing interaction between the single-site Kon-

do effect and intersite coupling.[10,11] Above 65 K $\Delta\alpha_V$ becomes negative, indicating a second contribution. Note that also in inelastic neutron scattering experiments[10] the (antiferro)magnetic correlations have been observed up to 70 K, and the metamagneticlike transition could be followed by magnetoresistivity experiments[8] up to about the same temperature. The second (negative) contribution has a minimum at 120 K, somewhat above the temperature where the second maximum in the excess specific heat[1] is observed (84 K). We attribute this anomaly to a crystal-field effect. Before analyzing the two contributions we shall discuss the data in terms of Grüneisen parameters.

A. Grüneisen parameters

For a particular contribution to the thermal properties a physically meaningful Grüneisen relation emerges when the entropy S_i can be written as $S_i[T/T_i(V)]$, where $T_i(V)$ is a volume-dependent characteristic term of the entropy term. The coefficient of volume expansion for this contribution is given by

$$\alpha_V=-\frac{1}{V}\left[\frac{\partial S_i}{\partial P}\right]_T=-\kappa\left[\frac{\partial^2 F_i}{\partial V\partial T}\right], \tag{1}$$

where F_i is the free energy and $\kappa=-1/V(\partial V/\partial P)_T$ is the isothermal compressibility. The molar specific heat (at constant volume) is given by

$$c_V=T\left[\frac{\partial S_i}{\partial T}\right]_V=-T\left[\frac{\partial^2 F_i}{\partial T^2}\right]_V. \tag{2}$$

The Grüneisen parameter for this particular entropy term is then defined by

$$\Gamma_i=\frac{V_m\alpha_V}{\kappa c_V}=-\frac{\partial \ln T_i(V)}{\partial \ln V}, \tag{3}$$

where V_m is the molar volume. Often several processes contribute to α. Therefore, it is convenient to define an effective Grüneisen parameter

$$\Gamma_{\text{eff}}=\frac{V_m\alpha_V(T)}{\kappa c(T)}=\sum_i \Gamma_i\frac{c_i(T)}{c(T)}. \tag{4}$$

Γ_{eff} is then an experimental parameter which is, in general, temperature dependent. In a first attempt to analyze Γ_{eff} it can be written as a sum of the products of the temperature independent Γ_i's and the fractional specific heats $c_i(T)/c(T)$. If Γ_{eff} is constant in a certain temperature interval, one can identify Γ_{eff} with the Grüneisen parameter for the particular mechanism that governs the thermal properties in that temperature range.

In the following we calculate the effective electronic Grüneisen parameter, Γ_{el}, that results after separating out the phonon contributions to c and α, as obtained from measurements on $LaRu_2Si_2$ (the conduction-electron contribution of $LaRu_2Si_2$ can be neglected). The f-electron specific heat $\Delta c(T)$, has been measured by Besnus *et al.* (Ref. 1). Their data are reproduced in Fig. 5.

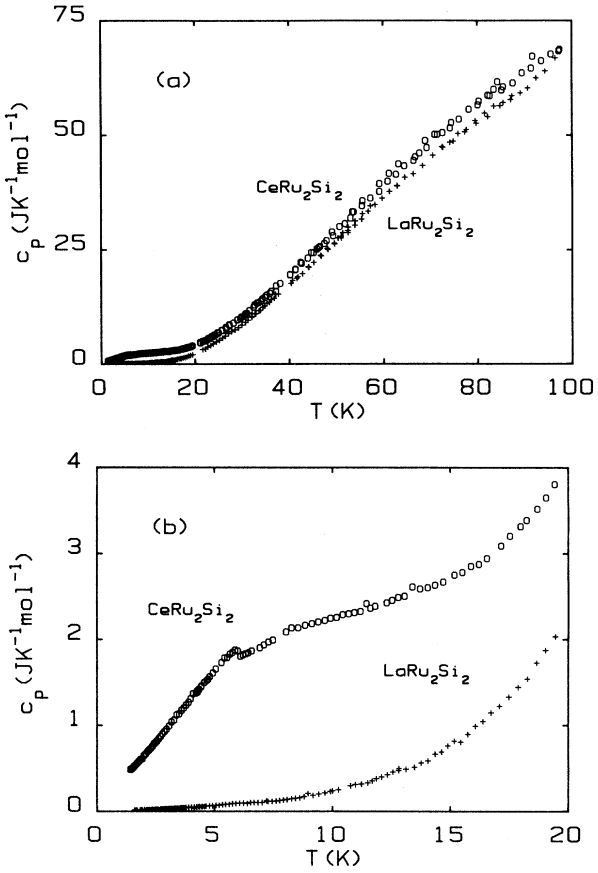

FIG. 5. Specific heat of $CeRu_2Si_2$ (○) and $LaRu_2Si_2$ (+); (a) below 100 K and (b) below 20 K (after Ref. 1).

At this moment a few remarks concerning the possible errors in $\Delta c(T)$ and $\Delta\alpha(T)$ need to be made. First, we note that the thermal-expansion and specific-heat experiments have been performed on different samples. The existing specific-heat data[1-4] are somewhat at variance with each other, which possibly indicates a slight sample dependence. Second, we notice that the scatter in the high-temperature limit of the specific-heat data is considerable [Fig. 5(a)], putting a large error bar on the values for Δc. In view of this large error bar, one cannot exclude that the maximum in Δc would be found above 100 K, as suggested by the observed minimum in $\Delta\alpha$ (at 120 K). Third, due to the large thermal dilatation, the difference between the specific heat at constant pressure, c_P, and at constant volume, c_V, given by

$$c_P-c_V=\frac{\alpha_V^2 V_m T}{\kappa} \tag{5}$$

is not negligible anymore. In Fig. 6 we show results for c_P-c_V, using a value for κ of 0.95 Mbar^{-1} (Ref. 18). The correction to the measured electronic specific heat Δc_P becomes of the order of 10% at 11 K. In the following analysis this correction has not been taken into account in view of the aforementioned uncertainties. However,

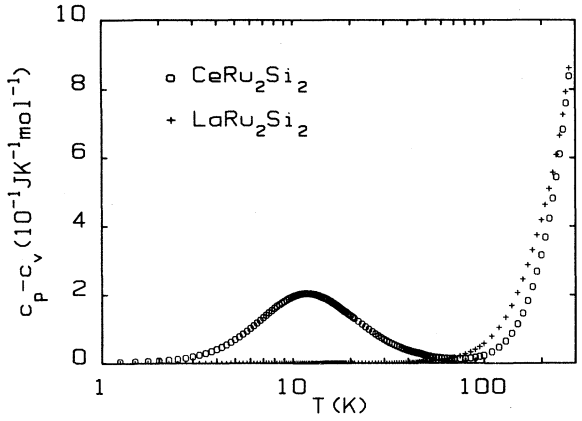

FIG. 6. $c_P - c_V$ for $CeRu_2Si_2$ (○) and $LaRu_2Si_2$ (+).

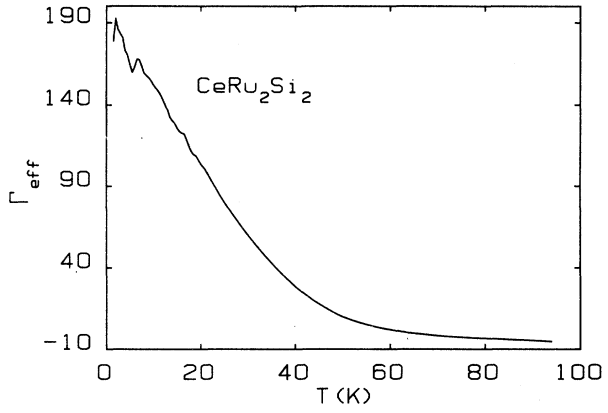

FIG. 7. Γ_{eff} vs T for $CeRu_2Si_2$ (after subtraction of the phonon contribution).

when performing a more precise analysis this correction becomes important. Care should also be taken when performing specific-heat measurements as function of pressure on $CeRu_2Si_2$. We note, furthermore, that the uncorrected c_P leads to a small overestimation of the involved entropy.

In Fig. 7 we present Γ_{el} versus temperature. In the low-temperature limit Γ_{el} reaches the huge value of 190. Retaining only the linear terms ($T \to 0$) $\alpha_V = 3aT$ and $c = \gamma T$, where $a = 4.3 \times 10^{-6}$ K^{-2} and $\gamma = 0.35$ $\text{J/K}^2\text{mol}$, we obtain the heavy-fermion Grüneisen parameter

$$\Gamma_{\text{el}}(T \to 0) = \Gamma_{\text{hf}} = 3aV_m/\kappa\gamma = 190 \ .$$

With raising temperature, Γ_{el} rapidly drops (up to 25 K in a nearly linear way), becomes negative above 65 K, and levels off at a value of -5.3. This plateau value can be taken as the crystal-field Grüneisen parameter Γ_{cf}, for the first-excited doublet. The unusually large value for Γ_{hf} implies a strong pressure dependence of the linear term in the specific heat

$$\frac{d\gamma}{dp} = -\kappa\Gamma_{\text{hf}}\gamma = -66 \text{ mJ/(mol K}^2\text{ kbar)} \ .$$

Similar large values for Γ_{hf} have previously been inferred from magnetic and transport data.[19] From the pressure dependence of the Pauli susceptibility[19] a value for Γ_{hf} of 180 was deduced. A same value has been derived from the pressure dependence of the coefficient of the T^2 term in the resistivity.[19] Since the products $\chi(T \to 0)T_{\max}$ (where $T_{\max}$ is the temperature at which the maximum in χ is observed) and $\chi(H \to 0)H_{\max}$ (where $H_{\max} = H^*$ is the field at which the maximum in the differential susceptibility or the maximum in the magnetoresistance is observed) were both found to be (nearly) pressure independent, identical values for Γ_{hf} have been obtained from the pressure dependences of $T_{\max}$ and $H_{\max}$. Apparently, the thermal and magnetic Grüneisen parameters,[20]

$$\Gamma_T = -\frac{\partial \ln T^*}{\partial \ln V}, \quad \Gamma_H = -\frac{\partial \ln H^*}{\partial \ln V} \tag{6}$$

are identical for $CeRu_2Si_2$ (for $H \| c$ and $T \to 0$), which led Mignot *et al.* (Ref. 19) to conclude that the thermal and magnetic properties can be scaled by one single-energy parameter. It is interesting to note that Lehmann[21] has found a similar value $\Gamma_{\text{hf}} = 151$ in analyzing specific-heat data on pseudobinary $(Ce,La)Ru_2Si_2$ and $(Y,Ce)Ru_2Si_2$ alloys, that exhibit a chemical pressure induced variation of T^*. The large value for Γ_{hf} implies a strong volume dependence of the quasiparticle bands, and is a common feature for heavy-fermion systems.[14]

The negative value for Γ_{cf} implies that the first crystal-field splitting, Δ, decreases with pressure at a rate of

$$\frac{d\Delta}{dP} = \kappa\Gamma_{\text{cf}}\Delta = -1.2 \text{ K/kbar} \ .$$

A value for $d\Delta/dP$ can also be deduced from resistivity data,[2,22] assuming that the temperature at which the maximum in $\rho(T)$ occurs (after subtracting $LaRu_2Si_2$) indicates Δ/k_B. From the data in Ref. 22 it follows that $T_{\max}$ decreases from 250 to 225 K by applying 7.7 kbar, hence $d\Delta/dP = -3.2$ K/kbar.

B. Crystal-field model

In the case of tetragonal $CeRu_2Si_2$ the crystal symmetry splits the $J = \frac{5}{2}$ level into three double degenerate doublets. The appropriate level scheme as inferred from specific-heat data[1] is given by 0-220-1000 K. Because of the large energy separation between the first- and second-excited doublet, we may assume that $CeRu_2Si_2$ is a two-level system in the investigated temperature range. The free energy (per mole) for such a two-level system is given by

$$F = -RT \ln(g_0 + g_1 e^{-\Delta/T}) \ , \tag{7}$$

where $g_0 = g_1 = 2$ are the degeneracies and Δ is the energy splitting (R is the gas constant). In general $\Delta = \Delta(T, V)$, but we here assume that $\Delta = \Delta(V)$. The population of the second level leads to the well-known Schottky anomaly in

the molar specific heat[23]

$$C_{\mathrm{Sch}}=R\left[\frac{\Delta}{T}\right]^2\frac{e^{\Delta/T}}{(1+e^{\Delta/T})^2}\ . \tag{8}$$

Since the entropy is a function of T/Δ, the equivalent expression for the thermal expansion follows directly from Eq. (1):

$$\alpha_{\mathrm{Sch}}=\frac{R\kappa}{V_m}\left[-\frac{\partial\ln\Delta}{\partial\ln V}\right]\left[\frac{\Delta}{T}\right]^2\frac{e^{\Delta/T}}{(1+e^{\Delta/T})^2} \tag{9}$$

with

$$\Gamma_{\mathrm{Sch}}=-\frac{\partial\ln\Delta}{\partial\ln V}=\frac{V_m\alpha_{\mathrm{Sch}}}{\kappa c_{\mathrm{Sch}}}\ . \tag{10}$$

In Fig. 8 we compare α_{el} with the curves calculated from Eq. (9), employing $\Gamma_{\mathrm{Sch}}=\Gamma_{\mathrm{cf}}=-5.3$ (see Fig. 7), and values for $\Delta=T_{\mathrm{min}}/0.417$ of 220 and 288 K. As mentioned above, from the specific-heat analysis $\Delta=220$ K was inferred. From the thermal-expansion data it follows that $\Delta=288$ K is more appropriate.

Another way to possibly get a handle on the crystal-field effects in tetragonal rare-earth compounds has recently been worked out by Morin *et al.* (Ref. 24). These authors have employed a susceptibility formalism for magnetic and quadrupolar interactions, that includes magnetoelastic coupling. The equilibrium values for the strains are obtained after minimizing the magnetoelastic energy with respect to the strains. In the tetragonal symmetry the coefficients of expansion are then given by

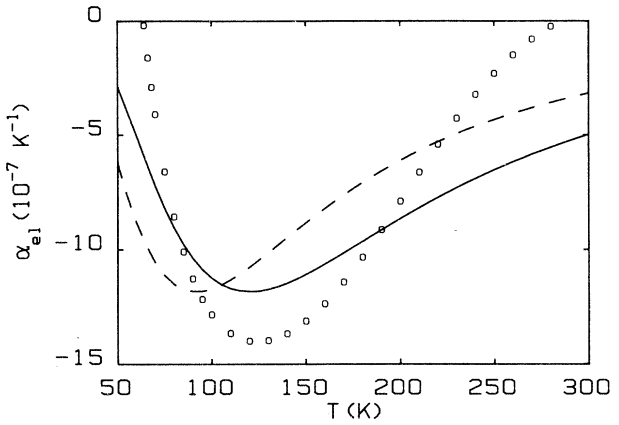

FIG. 8. α_{el} for $CeRu_2Si_2$. (○) Experimental points. Solid and dashed lines are calculated in a crystal-field model [Eq. (9)] with $\Gamma_{\mathrm{cf}}=-5.3$ and $\Delta=288$ and 220 K, respectively.

$$\alpha_{\parallel}=\frac{1}{\sqrt{3}}\frac{(C_0^{\alpha 2}B^{\alpha 1}-C_0^{\alpha 12}B^{\alpha 2})+\sqrt{2}(C_0^{\alpha 1}B^{\alpha 2}-C_0^{\alpha 12}B^{\alpha 1})}{C_0^{\alpha 1}C_0^{\alpha 2}-(C_0^{\alpha 12})^2}\frac{d\langle O_2^0\rangle}{dT}\ ,$$

$$\alpha_{\perp}=\frac{1}{\sqrt{3}}\frac{(C_0^{\alpha 2}B^{\alpha 1}-C_0^{\alpha 12}B^{\alpha 2})-\frac{1}{\sqrt{2}}(C_0^{\alpha 1}B^{\alpha 2}-C_0^{\alpha 12}B^{\alpha 1})}{C_0^{\alpha 1}C_0^{\alpha 2}-(C_0^{\alpha 12})^2}\frac{d\langle O_2^0\rangle}{dT}\ . \tag{11}$$

Here, $C_0^{\alpha 1}$, $C_0^{\alpha 2}$, and $C_0^{\alpha 12}$ are functions of the background elastic constants (without the crystal-field effects), $B^{\alpha 1}$ and $B^{\alpha 2}$ are magnetoelastic coupling parameters, and O_2^0 is a quadrupolar operator. From Eq. (11) it follows that $\alpha_{\parallel}$ and $\alpha_{\perp}$ have the same temperature dependence. When fitting Eq. (11) to the experimental data, $B^{\alpha 1}$ and $B^{\alpha 2}$ can be determined if all the elastic constants C_0^i are known. Since this is not the case, we restrict ourselves to the temperature dependence that is determined by $d\langle O_2^0\rangle/dT$ alone. Therefore, we have normalized α_{el} to -1 at $T_{\mathrm{min}}=120$ K. In Fig. 9 we show the results, calculated with Eq. (11) where we used $\Delta=288$ K, and $\langle O_2^0\rangle$ was calculated using the states[21]

$$|0\rangle=a|\pm\tfrac{5}{2}\rangle-b|\mp\tfrac{3}{2}\rangle\ ,$$

$$|1\rangle=|\pm\tfrac{1}{2}\rangle\ ,$$

and

$$|2\rangle=b|\pm\tfrac{5}{2}\rangle+a|\mp\tfrac{3}{2}\rangle\ ,$$

with $a=0.96$ and $b=(1-a^2)^{1/2}$. For comparison we

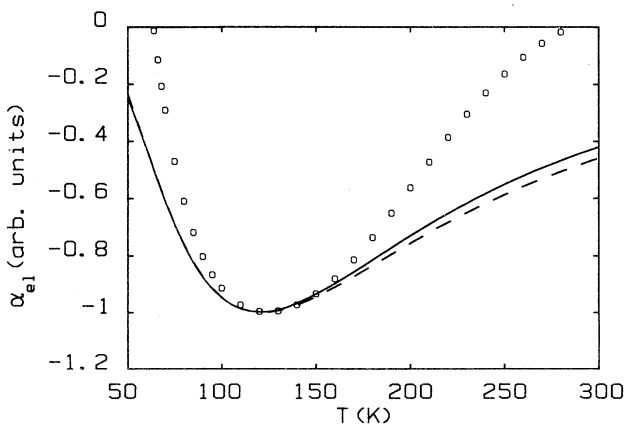

FIG. 9. α_{el} for $CeRu_2Si_2$ normalized to -1 at 120 K. (○) Experimental points. The dashed line is calculated using Eq. (11). The solid line is calculated using Eq. (9) with $\Gamma_{\mathrm{cf}}=-5.3$ and $\Delta=288$ K.

also show the results for the pure Schottky anomaly [Eq. (9)] in Fig. 9. Apparently, including magnetoelastic coupling does not include the quality of the crystal-field fit.

C. Resonance-level model

In the single-ion Kondo problem the interaction of the impurity spin with the conduction electrons leads to a resonance at the Fermi level. Although $CeRu_2Si_2$ belongs to the class of Kondo-lattice compounds, we shall, in a first attempt to describe the low-temperature thermal-expansion data, use a simple resonance-level model as explored by Schotte and Schotte.[25] In this model a resonance of Lorentzian shape is formed at the Fermi energy. The width (Δ) of the resonance is in the order of the Kondo temperature $\Delta \simeq k_B T_K$. The resonance leads to an additional free energy

$$F = -RT \int_{-\infty}^{+\infty} \rho(\varepsilon) \ln(1+e^{-\varepsilon/k_B T}) d\varepsilon \ , \tag{12}$$

where

$$\rho(\varepsilon) = \frac{\Delta}{\pi} \frac{1}{(\varepsilon^2+\Delta^2)} \ . \tag{13}$$

The specific heat for this contribution at zero magnetic field and for spin $\frac{1}{2}$ is given by[25]

$$C_{SS} = \frac{R}{\pi} \frac{\Delta}{T} \left[1 - \frac{1}{2\pi k_B} \left[\frac{\Delta}{T} \right] \psi' \left[\frac{1}{2} + \frac{\Delta}{2\pi k_B T} \right] \right] , \tag{14}$$

where $\psi'(z) = d \ln\Gamma(z)/dz$ is the digamma function. Since, in this case, the entropy is also a function of T/Δ the equivalent expression for the volume expansion is given by

$$\alpha_{SS} = \frac{\kappa}{V_m} \frac{R}{\pi} \left[-\frac{\partial \ln\Delta}{\partial \ln V} \right] \frac{\Delta}{T} \left[1 - \frac{1}{2\pi k_B} \left[\frac{\Delta}{T} \right] \psi' \times \left[\frac{1}{2} + \frac{\Delta}{2\pi k_B T} \right] \right] \tag{15}$$

[as may also be verified by inserting the free energy in Eq. (1)], where $\Delta = \Delta(V)$. For the resonance-level model we have

$$\Gamma_{SS} \equiv -\frac{\partial \ln\Delta}{\partial \ln V} = -\frac{\partial \ln T_K}{\partial \ln V} = \frac{V_m \alpha_{SS}}{\kappa c_{SS}} \ . \tag{16}$$

In Fig. 10 we compare Eq. (15) with the experimental data. Assuming $\Gamma_{SS} = \Gamma_{hf} = 190$, and with a value for T_K of 19 K, we get remarkably good results in the low-temperature range, in view of the simplicity of the model. In Fig. 11 the calculated and experimental specific heat are compared, using the same value $T_K = 19$ K.

D. Scaling behavior

Puech *et al.* (Ref. 9) and Mignot *et al.* (Ref. 19) have shown that in the case of $CeRu_2Si_2$ the expression for the free energy can be written as a function of one single scaling parameter at low temperatures. Thus, for instance,

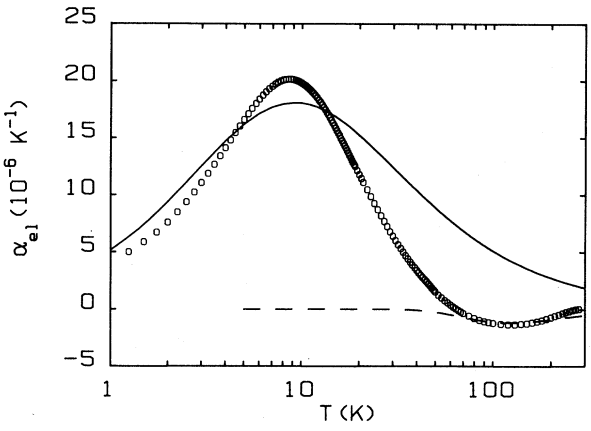

FIG. 10. α_{el} for $CeRu_2Si_2$. (○) Experimental points. The solid line is calculated in a resonance-level model [Eq. (15)] with $\Gamma_{SS} = 190$ K and $T_K = 19$ K. The dashed line is a crystal-field fit [Eq. (9)] with $\Gamma_{cf} = -5.3$ and $\Delta = 288$ K.

the magnetization can be written as $M(H,P) = f[H/H^*(P)]$, where H^* is the pressure-dependent critical field for the metamagneticlike transition. This scaling law was also checked by comparing the volume magnetostriction with the differential susceptibility, according to[9]

$$\left[\frac{\partial V}{\partial H} \right]_{P,T} = H \frac{\partial \ln H^*}{\partial P} \left[\frac{\partial M}{\partial H} \right]_{P,T} , \tag{17}$$

where

$$\frac{\partial \ln H^*}{\partial P} = -\frac{\partial \ln\chi(T \to 0)}{\partial P}$$

since the product $H^*\chi(T \to 0)$ was found to be pressure independent. Since in Ref. 9 only relative magnetostriction measurements were presented (as the calibration of the device was rather poor) we here check Eq. (17) by

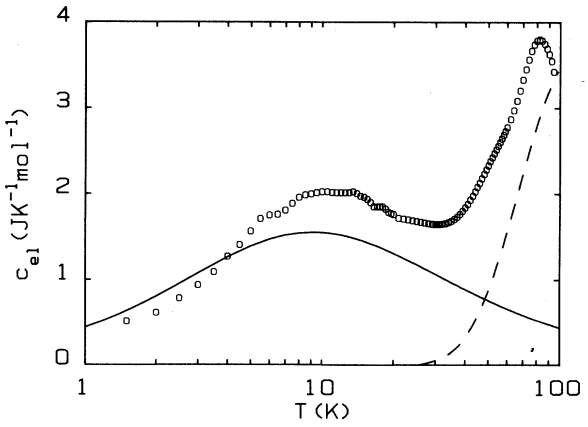

FIG. 11. Specific heat of $CeRu_2Si_2$. (○) Experimental points (after Ref. 1). The solid line is calculated in a resonance-level model [Eq. (14)] with a T_K of 19 K. The dashed line is a crystal-field fit [Eq. (8)] with $\Delta = 288$ K.

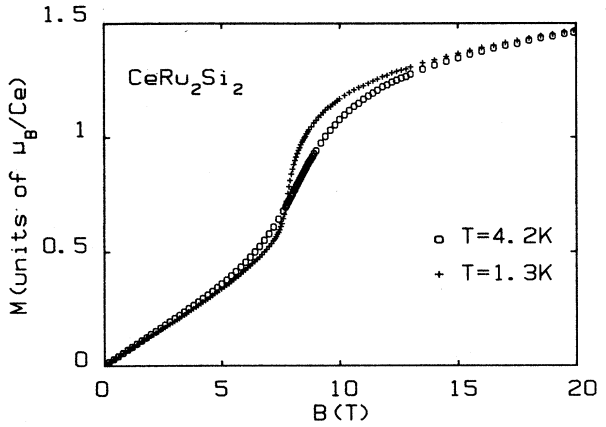

FIG. 12. Magnetization of $CeRu_2Si_2$ for a field direction along the c axis at a temperature of 1.3 K (+) and 4.2 K (○).

comparing the (absolute) volume magnetostriction (Fig. 3) with magnetization data (Fig. 12) on the same sample. The comparison is made in Fig. 13, where we used values for $\partial \ln\chi/\partial P$ of -188 and 167 Mbar^{-1}, at 4.2 and 1.3 K, respectively. The scaling is almost perfect at the lowest temperature (1.3 K).

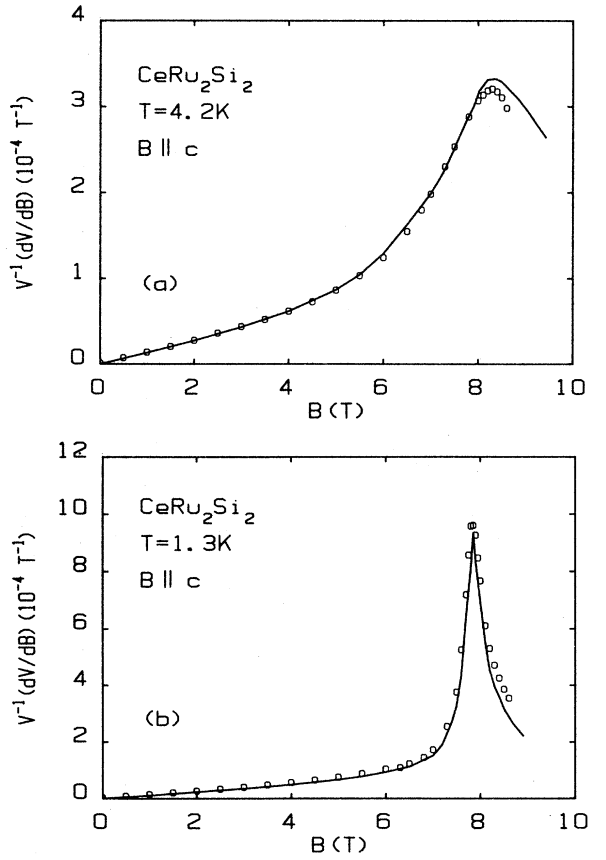

FIG. 13. Differential susceptibility of $CeRu_2Si_2$ ($B \| c$) as measured (○), and calculated using Eq. (17) (see text); (a) at 4.2 K and (b) at 1.3 K.

V. DISCUSSION AND SUMMARY

In a first approximation the thermal expansion and the specific heat of $CeRu_2Si_2$ can be explained by (*i*) at low temperatures a resonance-level model with an effective Kondo temperature $T_K \cong 19$ K, and (*ii*) at high temperatures a Schottky anomaly ($\Delta = 288$ K). The admixture of the Kondo and crystal-field effect leads, in the model of Hanzawa *et al.*,[26] to an effective Kondo temperature for the full multiplet of

$$T_K^h = (T_K \Delta_1 \Delta_2)^{1/3} \cong 170 \text{ K} ,$$

which possibly explains the remaining discrepancy between the crystal-field fit and experiment (see Fig. 8). On the other hand, the question can be raised whether the negative value of the crystal-field Grüneisen parameter is not a consequence of the interplay between the bare crystal-field and Kondo effect, leading to an apparent decrease of Δ with pressure, as T_K will certainly increase drastically with pressure. Inelastic neutron scattering experiments[27] were unsuccessful in demonstrating crystal-field excitations in $CeRu_2Si_2$, a feature often observed in heavy-fermion compounds, indicating a considerable effective broadening of the crystal-field levels.

The extrapolated ratio of α and c leads to a huge Grüneisen parameter $\Gamma_{el}(T \to 0) = 190$. As mentioned, large values have also been observed for other heavy-fermion systems, e.g., for $CeCu_6$, URu_2Si_2, UBe_{13}, and UPt_3 Γ_{hf} amounts to 57, 25, 34, and 71, respectively (Ref. 14). The particularly large value of Γ_{hf} for $CeRu_2Si_2$ is likely connected with the proximity of a low-temperature magnetic instability (see below). However, we cannot exclude that in the present highly anisotropic (uniaxial) case of $CeRu_2Si_2$ the electronic behavior is governed by a parameter that depends on one particular crystallographic direction (c axis), and not on the volume. In this respect we emphasize the large maximum of the relative variation of c/a at $T \sim 50$ K after subtracting the phonon contribution (Fig. 2).

A main result from the present experiments is the strong, almost linear, temperature dependence of Γ in the low-temperature range. Even at the lowest temperature ($T = 1.3$ K) no indication of a low-temperature regime where $\Gamma(T)$ reaches a constant has been observed. This clearly implies that the use of only one scaling parameter must be a crude approximation. Note that a sensitive physical property like the thermoelectric power,[28] Q, shows additional anomalies below 1 K (i.e., a maximum of Q at 1 K).

Inelastic neutron scattering experiments[10,11] reveal the presence of a strong interplay between (i) on-site correlations related with local Kondo fluctuations weakly dependent on the magnetic field, and (ii) intersite correlations that collapse in an applied field of $H^* = 8$ T. This shows that the metamagneticlike transition is associated with a drastic change of magnetic correlations. It is obvious that the ferromagnetic component will play a main role in the low-energy excitation spectrum at H^*, but this component has not been studied dynamically yet. Another important result from the neutron scattering experiments is that at low temperatures the (inelastic) energy

spectrum of the intersite coupling must be described by two parameters, an energy shift $\hbar\omega_0 \sim 1.2$ meV and linewidth $\Gamma_{is} \sim 0.9$ meV, whereas the single-site contribution appears as a quasielastic type with linewidth $\Gamma_{ss} \sim 2$ meV. Thus the underlying microscopic nature of $CeRu_2Si_2$ is clearly complex, which leads to the difficulties in interpreting the thermal behavior, notably when comparisons are made between different variables as an observable (c) and its pressure derivative (α), that are both sensitive to the proximity of an instability. Studies[29] of the alloy system $Ce_{1-x}La_xRu_2Si_2$ show that the long-range magnetic versus paramagnetic instability occurs for $x \sim 0.08$, which converted in terms of pressure corresponds to a negative (chemical) pressure of 2.0 kbar. Assuming a continuity of the properties in the series of $Ce_{1-x}La_xRu_2Si_2$ compounds, it is evident that $CeRu_2Si_2$ is close to magnetic instability. The instability leads to the strong competing interactions and to the huge Grüneisen parameter for $T \to 0$ K, and, correlatively, to the large crossover regime. Let us emphasize that the idea of continuity may be incorrect, since the perfect-lattice case may differ from the alloy problem when a sufficient purity of materials is realized. From neutron work on UPt_3 (Ref. 30) and on substituted alloys,[31] $U(Pt_{1-x}Pd_x)_3$, it is clear that the perfect-lattice case ($T_N \sim 5$ K with a very weak ordered moment $m_0 \sim 0.02\mu_B$) is not a simple extrapolation of the alloy situation (for $x = 0.05$, $T_N \sim 6$ K with an ordered moment of $0.5\mu_B$).

Despite the difficulty to explain quantitatively the temperature variation of the Grüneisen parameter Γ, it is intriguing to see the excellent agreement between different values of Γ, either extrapolated from thermal studies, or derived from the pressure dependence of the magnetic or transport properties (see Sec. IV D). This suggests that one main energy (depending on pressure) governs the situation. Thus, a reduction of the just-described complex behavior may be found in the bare mechanism. The dominant effect may be the local fluctuations (Kondo effect or on-site Coulomb coupling). The intersite exchange might basically originate from the light electrons, before the heavy-quasiparticle bands are built at low temperatures. In contrast to the case of itinerant nearly ferromagnetic magnetism of the $3d$ elements, the energy width of the wave-vector response at any wave vector will always be finite due to the local fluctuations and never collapse. Experimentally, scaling is generally found in the paramagnetic regime, despite evidences that competing interactions occur. An excellent example in this respect is the scaling law for the magnetoresistivity data in UBe_{13} (Ref. 32).

We notice that the large value of the electronic Grüneisen parameter ($\Gamma = 190$) and the relatively low value of the crystal-field Grüneisen parameter ($\Gamma_{cf} = -5.3$) are inversely connected with the strength of their characteristic energies (19 and 288 K). The interesting point is that the huge electronic Grüneisen parameter corresponds to a huge effective mass, i.e., to a low characteristic energy. The ratio of Γ over the mass enhancement which gives the absolute variation of the characteristic energy is a rather normal number, i.e., not enhanced by a large factor. This confirms indirectly that the mass enhancement arises firstly from a renormalization effect, producing noninteracting heavy quasiparticles, and secondly from the interaction between these renormalized quasiparticles. Both effects have a comparable size.

It would be interesting to investigate the thermal properties of $CeRu_2Si_2$ employing a resonance-level model that includes intersite coupling, as, for instance, is developed by Matho and Marcenat.[33] In the system $Ce_{1-x}La_xRu_2Si_2$ long-range antiferromagnetic order occurs in the concentration range $0.08 \leq x \leq 0.9$, with a maximum Néel temperature of 6 K.[29] The evolution of the large low-temperature anomaly for nonordered $CeRu_2Si_2$ into a negative peak (at T_N) for the doped ordered compounds is, at present, under investigation.

In summary, we have presented thermal-expansion measurements on single-crystalline samples of heavy-fermion $CeRu_2Si_2$ and its nonmagnetic analog $LaRu_2Si_2$. The high-temperature part of the measurements is described with a Schottky anomaly yielding $\Delta = 288$ K. In a first attempt to analyze the low-temperature f-electron contribution we used a simple resonance-level model, yielding $T_K = 19$ K. As the low-temperature magnetic excitation spectrum reveals competing magnetic interactions, the analysis with one scaling parameter should be taken with some caution. The Grüneisen parameter of $CeRu_2Si_2$ has a linear temperature dependence below 25 K and attains an exceptionally large value ($\Gamma_{hf} = 190$) in the low-temperature limit. Its strong temperature dependence suggests that the reduction to one scaling parameter will be realized only at very low temperatures.

ACKNOWLEDGMENTS

The authors have largely benefited from discussions with J. Pierre, D. Schmitt, and K. Matho. M. J. Besnus is gratefully acknowledged for communicating the specific-heat data. The work of A.d.V. has been made possible by financial support from the Royal Netherlands Academy of Arts and Sciences. A.L. was supported by Conselho Nacional de Desenvolvimento Cientifico e Tecnologico, Brazil (CNPq).

*Also at Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65, 1018XE Amsterdam, The Netherlands.

[1] M. J. Besnus, J. P. Kappler, P. Lehmann, and A. Meyer, Solid State Commun. **55**, 779 (1985).

[2] J. D. Thompson, J. O. Willis, C. Godart, D. E. MacLaughlin, and L. C. Gupta, Solid State Commun. **56**, 169 (1985).

[3] F. Steglich, U. Rauchschwalbe, U. Gottwick, H. M. Mayer, G. Sparn, N. Grewe, U. Poppe, and J. J. M. Franse, J. Appl. Phys. **57**, 3054 (1985).

[4]R. A. Fisher, N. E. Phillips, C. Marcenat, J. Flouquet, P. Haen, P. Lejay, and J. M. Mignot, J. Phys. (Paris) Colloq. **49**, C8-759 (1988).
[5]L. C. Gupta, D. E. MacLaughlin, Cheng Tien, C. Godart, M. A. Edwards, and R. D. Parks, Phys. Rev. B **28**, 3673 (1983).
[6]J. L. Tholence, P. Haen, D. Jaccard, P. Lejay, J. Flouquet, and H. F. Braun, J. Appl. Phys. **57**, 3172 (1985).
[7]L. E. DeLong, Phys. Rev. B **33**, 3556 (1986).
[8]P. Haen, J. Flouquet, F. Lapierre, P. Lejay, and G. Remenyi, J. Low Temp. Phys. **67**, 391 (1987).
[9]L. Puech, J. M. Mignot, P. Lejay, P. Haen, J. Flouquet, and J. Voiron, J. Low Temp. Phys. **70**, 237 (1988).
[10]L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, P. Lejay, and J. Flouquet, Phys. Rev. B **38**, 4481 (1988).
[11]J. Rossat-Mignod, L. P. Regnault, J. L. Jaccoud, C. Vettier, P. Lejay, J. Flouquet, E. Walker, D. Jaccard, and A. Amato, J. Magn. Magn. Mater. **76&77**, 376 (1988).
[12]A. de Visser, A. Menovsky, and J. J. M. Franse, Physica **147B**, 81 (1987).
[13]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. **113A**, 489 (1986).
[14]A. de Visser, J. J. M. Franse, and J. Flouquet, Proceedings of the International Symposium on Magnetoelasticity and Electronic Structure of Transition Metals, Alloys and Films, Duisburg, 1989 [Physica **B**, in press].
[15]A. de Visser, P. Haen, P. Lejay, and J. Flouquet, J. Phys. (Paris) Colloq. **49**, C8-767 (1988).
[16]R. Ballestracci and G. Astier, C.R. Acad. Sci. Paris **286**, B109 (1978).
[17]A. de Visser, Ph.D. thesis, University of Amsterdam, 1986.
[18]J. M. Laurant and M. Rossignol (private communication).
[19]J. M. Mignot, J. Flouquet, P. Haen, F. Lapierre, L. Puech, and J. Voiron, J. Magn. Magn. Mater. **76&77**, 97 (1988).
[20]A. B. Kaiser and P. Fulde, Phys. Rev. B **37**, 5357 (1988).
[21]P. Lehmann, Ph.D. thesis, Université Louis-Pasteur, 1987.
[22]A. Ponchet, Ph.D. thesis, Université de Grenoble, 1987; J. M. Mignot *et al.*, Phys. Rev. B (to be published).
[23]E. S. R. Gopal, *Specific Heat at Low Temperatures* (Heywood, London, 1966), p. 102.
[24]P. Morin, J. Rouchy, and D. Schmitt, Phys. Rev. B **37**, 5401 (1988).
[25]K. D. Schotte and U. Schotte, Phys. Lett. **55A**, 38 (1975).
[26]K. Hanzawa, K. Yamada, and K. Yosida, J. Magn. Magn. Mater. **47&48**, 357 (1987).
[27]A. Severing, E. Holland-Moritz, B. D. Rainford, S. R. Culverhouse, and B. Frick, Phys. Rev. B **39**, 2557 (1989).
[28]A. Amato, D. Jaccard, J. Sierro, F. Lapierre, P. Haen, P. Lejay, and J. Flouquet, J. Magn. Magn. Mater. **76&77**, 263 (1988).
[29]P. Haen, J. P. Kappler, F. Lapierre, P. Lehmann, P. Lejay, J. Flouquet, and A. Meyer, J. Phys. (Paris) Colloq. **49**, C8-757 (1988).
[30]G. Aeppli, E. Bucher, C. Broholm, J. K. Kjems, J. Baumann, and J. Hufnagel, Phys. Rev. Lett. **60**, 615 (1988).
[31]P. Frings, B. Renker, and C. Vettier, Physica B **151**, 499 (1988).
[32]B. Batlogg, D. J. Bishop, E. Bucher, B. Golding, Jr., A. P. Ramirez, Z. Fisk, J. L. Smith, and H. R. Ott, J. Magn. Magn. Mater. **63&64**, 441 (1987).
[33]K. Matho and C. Marcenat, J. Phys. (Paris) Colloq. **49**, C8-717 (1988).