Calorimetric and transport investigations of CePd$_{2+x}$Ge$_{2-x}$ ($x = 0$ and 0.02) up to 22 GPa

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The influence of pressure on the magnetically ordered CePd$_{2.02}$Ge$_{1.98}$ has been investigated by a combined measurement of electrical resistivity, $\rho(T)$, and ac-calorimetry, $C(T)$, for temperatures in the range $0.3 \, K < T < 10 \, K$ and pressures, $p$, up to 22 GPa. Simultaneously CePd$_{2.02}$Ge$_{1.98}$ has been examined by $\rho(T)$ down to 40 mK. In CePd$_{2.02}$Ge$_{1.98}$ and CePd$_2$Ge$_2$ the magnetic order is suppressed at a critical pressure $p_c = 11.0$ GPa and $p_c = 13.8$ GPa, respectively. In the case of CePd$_{2.02}$Ge$_{1.98}$ not only the temperature coefficient of $\rho(T)$, $\alpha$, indicates the loss of magnetic order but also the ac-signal $1/V_{ac} \propto C/T$ recorded at low temperature. The residual resistivity is extremely pressure sensitive and passes through a maximum and then a minimum in the vicinity of $p_c$. The $(T, p)$ phase diagram and the $A(p)$-dependence of both compounds can be qualitatively understood in terms of a pressure-tuned competition between magnetic order and the Kondo effect according to the Doniach picture. The temperature–volume $(T, V)$ phase diagram of CePd$_2$Ge$_2$ combined with that of CePd$_{2}$Si$_2$ shows that in stoichiometric compounds mainly the change of interatomic distances influences the exchange interaction. It will be argued that in contrast to this the much lower $p_c$-value of CePd$_{2.02}$Ge$_{1.98}$ is caused by an enhanced hybridization between $4f$ and conduction electrons.

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I. INTRODUCTION

The application of external pressure on metals with strong correlations is an established technique to tune their ground state properties. The electronic interactions in heavy-Fermion (HF) compounds can be influenced in such a way that high pressure favors the Kondo interaction in Ce-compounds [1, 2, 3, 4, 5] and the RKKY interaction in Yb-systems [6, 7, 8, 9, 10] and thus, pressure suppresses (favors) long range magnetic order and enhances (weakens) the screening of the localized $4f$-electrons. If both interactions are of similar strength in the vicinity of a critical pressure $p_c$ often a deviation from the Fermi-liquid (FL) behavior is observed and some Ce-compounds even attain a superconducting ground state.

Electrical resistivity measurements as a function of temperature, $\rho(T)$, are the standard method to explore the low temperature phase diagram of HF systems up to pressures $p \approx 20 \, GPa$. It is desirable to measure thermodynamic quantities, notably the specific heat $C(T)$ in these extreme conditions. The accessible pressure range for specific heat experiments was limited to 2-3 GPa since adiabatic techniques demand large sample masses and thus, a large cell volume. For an anvil-type of high pressure cell a much smaller sample volume is required, which makes an adiabatic measurement a hopeless venture. Among the non-adiabatic (or dynamic) methods, ac-calorimetry [12, 13] is a suitable technique to be used at high pressures. Very high sensitivity can be achieved, whereas the absolute accuracy is less than for adiabatic techniques.

A major step towards measuring $C(T)$ under extreme conditions has been achieved by implementing the ac-calorimetry in a Bridgman-type of pressure cell suited for 10 GPa [14]. The sample was embedded in a soft mineral (steatite) and an ac-current was supplied to a heater close to the sample. The experimental findings have been confirmed by an independent study using a diamond anvil cell with He as pressure transmitting medium and laser heating [15, 16]. Motivated by these results we assembled the ac-calorimetry in a Bridgman-type of high pressure cell capable of reaching 25 GPa and temperatures of the order of 30 mK [17].

So far, only CeCu$_2$Ge$_2$ and CeRu$_2$Ge$_2$, where Ge is an isoelectronic substitute for Si, have been studied extensively under pressure. The former compound exhibits a phase diagram similar to that of CeCu$_2$Si$_2$ but shifted by 9.4 GPa [18]. Close to the critical pressure, $p_c$, the long range magnetic order is suppressed and superconductivity appears like in CeCu$_2$Si$_2$ at low pressure [19].

The temperature–volume $(T, V)$ phase diagram of CeRu$_2$Ge$_2$ is identical to that of the solid-solution CeRu$_2$(Si$_{1-x}$Ge$_x$)$_2$. In contrast to CeCu$_2$Ge$_2$ no superconductivity is observed around the magnetic/non-magnetic borderline as in CeRu$_2$Si$_2$ at ambient pressure. These observations support the notion that the Ge-substitution mainly has the effect of reducing the hybridization between the $4f$ and conduction electrons due...
to the expansion of the unit cell volume. This argument seems not to be limited to compounds crystallizing in the ThCr$_2$Si$_2$-type of structure. Another example is the magnetically ordered CeCu$_2$Au, which can be pressure-tuned into a non-magnetic ground state, analogous to the HF prototype CeCu$_6$ at ambient pressure [1]. The pressure study revealed a deviation from FL behavior and a low temperature anomaly in $\rho(T)$ close to $p_c$, which could be interpreted as faint traces of a superconducting state [3].

All these studies have in common that pressure has been applied to stoichiometric compounds. Small deviations from stoichiometry are believed to result in strong effects on the electronic correlations. Detailed investigations of the influence of Ni-excess in Ce$_{1.005}$Ni$_{2+x}$Ge$_{2-x}$ have shown that a low residual resistivity, $\rho_0$, is a crucial requirement for the occurrence of incipient superconductivity at ambient pressure [24] and that the transition temperature can be shifted upwards by carefully adjusting the Ni excess [21]. For the stoichiometric sample, however, pressure had to be applied to achieve superconductivity [21]. The combination of these results has led to the hypothesis that an enhanced hybridization due to an electronically different environment of the Ce-ions is a crucial ingredient to reduce $p_c$ and to achieve a superconducting ground state.

In this article we report on results of $\rho(T)$ as well as ac-calorimetry experiments on CePd$_2$Ge$_2$ and $\rho(T)$ measurements on CePd$_{2.02}$Ge$_{1.98}$ performed in one pressure experiment. CePd$_2$Ge$_2$ enters an antiferromagnetically ordered phase at $T_N \approx 5.1$ K [23, 24, 25, 26]. Its Si-counterpart, the HF system CePd$_2$Si$_2$ exhibits a similar magnetic structure with $T_N \approx 10$ K [23, 25]. Several groups have confirmed the occurrence of a superconducting ground state if the magnetic order is suppressed by external pressure ($p_c = 2.8$ GPa) [3, 1, 22, 24, 21, 22]. If the change of interatomic distances is the main source of altering the exchange coupling between 4$f$ and conduction electrons, $J$, then CePd$_2$Ge$_2$ should reveal a pronounced variation of $T_N(p)$. The interest in high pressure studies on CePd$_{2.02}$Ge$_{1.98}$ is to explore the role of stoichiometry on $J$ and thus on $p_c$. Measuring simultaneously $C(T)$ and $\rho(T)$ has the advantage that independent information about the strength of electronic correlations from the same specimen can be obtained.

In order to draw a credible conclusion about the pressure response of both compounds, it is essential to expose both samples to the same pressure conditions. The best way to achieve this is to place both specimens adjacent to each other in the same pressure cell.

### II. EXPERIMENTAL DETAILS

#### A. Sample Preparation and Characterization

The CePd$_{2+x}$Ge$_{2-x}$ compounds have been prepared by melting Ce (4N), Pd (5N), and Ge (6N) according to the composition in an arc ($x = 0$) or an induction furnace ($x = 0.02$) under Ar (6N) atmosphere. The samples have been melted several times to achieve good homogeneity. Mass loss during melting and annealing (CePd$_{2.02}$Ge$_{1.98}$ at 1420 K and CePd$_2$Ge$_2$ at 1470 K for two days) was negligible. A part of the polycrystalline ingots has been analyzed by x-ray powder diffraction. The diffraction pattern contained only peaks according to the ThCr$_2$Si$_2$ structure ($I4/mmm$). The magnetic structure of CePd$_2$Ge$_2$ consists of ferromagnetic planes stacked antiferromagnetically along the [110]-direction with moments ($\mu = 0.85\mu_B$ at 1.8 K) parallel to the stacking direction [24, 23, 24]. No information about the magnetic structure of CePd$_{2.02}$Ge$_{1.98}$ is available but it is very likely that the small Pd-excess does not change the antiferromagnetic structure.

The measurements of the specific heat, dc-magnetic susceptibility, and electrical resistivity at ambient pressure revealed for both compounds a phase transition into an antiferromagnetically ordered phase at about 5.1 K (Tab. I). The low temperature specific heat ($0.3 K < T < 2 K$) can be described by the sum of an electronic ($\gamma T$) and a magnon-like $T^3$ part with a gap $\Delta$ in the excitation spectrum. The increased $\gamma$-value of the Pd-rich compound in respect to the stoichiometric one points to enhanced correlations. The $\gamma$ and $\Delta$ values of CePd$_2$Ge$_2$ obtained here are larger than those reported in Ref. [24] due to the enlarged temperature range accessible in the present study. However, the absolute values of $C_p$ at $T_N$ are almost the same. The entropy release at $T_N$ is $S/R \approx 0.8\ln 2$ and reaches $\ln 2$ at about 9 K for both compounds. The high temperature magnetic susceptibility can be described by a Curie-Weiss law $\chi \propto \mu_{\text{eff}}/(T - \Theta)$, with an effective moment $\mu_{\text{eff}}$ close to the free moment value and $\Theta$ the Curie-Weiss temperature. The residual scattering is rather low in both compounds; the non-stoichiometric sample has the lower $\rho_0$-value.

#### TABLE I: Ambient pressure data of CePd$_{2.02}$Ge$_{1.98}$ and CePd$_2$Ge$_2$. The Néel temperature $T_N$ is the mean value of specific heat, dc-magnetic susceptibility, and electrical resistivity measurements. The specific heat can be described by $C = \gamma T + \beta T^3 \exp(-\Delta/T)$ for $T < 2$ K. $\mu_{\text{eff}}$ is the effective magnetic moment, $\Theta$ the Curie-Weiss temperature, $\rho_0$ the residual resistivity, and RRR the ratio $\rho(295 \text{ K})/\rho_0$.

| Compound          | $a$ (Å)   | $c$ (Å)   | $\gamma$ (mJ/(mol K$^2$)) | $\Theta$ (K) | $\mu_{\text{eff}}$ (µB) at 300 K | $\rho(\mu$cm) | RRR |
|-------------------|-----------|-----------|-----------------------------|--------------|---------------------------------|----------------|-----|
| CePd$_{2.02}$Ge$_{1.98}$ | 3.399(7)  | 10.0343(19) | 101.5(5)                    | -24(5)       | 2.1                             | 1.4(1)         | 32(3) |
| CePd$_2$Ge$_2$    | 3.414(5)  | 10.0417(5) | 44(1)                       | -16(5)       | 2.5                             | 1.7(1)         | 29(3) |
B. High Pressure Set-Up

Samples with cross sections of $23 \times 59 \mu m^2$ ($x = 0$) and $22 \times 48 \mu m^2$ ($x = 0.02$) have been cut from the polycrystalline ingots and placed into the pressure chamber (internal diameter of 1 mm) \([4]\). A small piece of Pb served as pressure gauge \([33]\) and was connected in series to the samples for four-point measurements. The samples have been arranged in the pressure chamber in such a way that the crystallographic c-axis was parallel to the pressurizing force. For the ac-calorimetry measurements the sample itself was used as heater and was thermally excited by an oscillating heating power $P = P_0[1 + \cos(\omega t)]$, due to an applied ac-voltage of frequency $\omega/2$. At steady state it increases the sample temperature by $\Delta T$ above the bath temperature $T_0$. This temperature increase contains a time-independent offset $T_{dc} = P_0/\Lambda$, with $\Lambda$ the thermal conduction of the heat link between sample and pressure cell (to a first approximation: the pressure-transmitting medium, i.e., steatite). In ideal conditions the oscillatory part of $\Delta T$ is $T_{ac} = P_0/(\omega C_p)$ \([2]\). These temperature oscillations have been measured with a AuFe/Au thermocouple attached to the sample. The thermovoltage $V_{ac}$ arises from the temperature difference between the sample (at $T_0 + \Delta T$) and the edge of the sample chamber (at $T_0$) \([10]\).

The dynamic response of the sample involves two time constants $\tau_1 = C_p/\Lambda$ and $\tau_2$. The former expresses the thermal coupling between the sample and the temperature bath, whereas the latter represents a characteristic time for the sample to reach thermal equilibrium. When the measuring frequency fulfills the condition $\omega \tau_1 = 1 \gg \omega \tau_2$, the ac-technique yields the specific heat of the sample. In the course of the experiment this condition was checked at several temperatures and pressures. The frequencies used were in the range 750 Hz $\leq \omega \leq 3000$ Hz. The condition $\omega \tau_2 \ll 1$ is fulfilled for metals because they ensure high thermal conductivity within the sample.

The inverse of the recorded lock-in voltage $V_{ac}$ is proportional to $C/T$, since the temperature dependence of the absolute thermoelectrical power, $S(T) \propto T$, is a fairly good assumption at $T < 1$ K. Above this temperature the $S(T)$ dependence is certainly different and $1/V_{ac}$ has to be interpreted with caution. Nevertheless, the present set-up has several advantages. Firstly, it is possible to check whether a pronounced anomaly in $1/V_{ac}$ is related to the sample or not with an independent $\rho(T)$ measurement on the same sample; secondly, it excludes an additional source of pressure inhomogeneity due to a heater attached to the sample; and thirdly, internal temperature gradients can be reduced as much as possible.

With such an arrangement it is in principle possible to calibrate the AuFe/Au thermocouple up to very high pressure and over a wide temperature range \([32]\). Here, we have only determined $S(T)$ at 4.2 K and 1.0 K to get a rough estimate of the influence of pressure on $S(T)$ \([37]\). The obtained values of the absolute thermopower of AuFe at 4.2 K and 1.0 K at 12 GPa are about 20% smaller than the values at ambient pressure. These rather small changes show that the interpretation of the results reported in this work is not affected qualitatively if the ambient pressure values of $S(T)$ are used.

The sample chamber has been carefully re-examined after pressure release to rule out changes in the positions of the voltage leads connected to the samples. The overall shape of the pressure cell as well as its initial diameter were almost unchanged and the distance between the voltage leads increased by less than 5%. Taking this uncertainty in the geometrical factor as well as the change in volume at high pressure into account the absolute value of $\rho(T)$ can be determined within 20%.

III. RESULTS

A. Transport measurements

The entrance into the magnetically ordered state is clearly visible by a cusp in $\rho_{mag}(T)$ of CePd$_{2}$Ge$_{1.98}$ and CePd$_{2}$Ge$_{2}$ (Fig. 1 and Fig. 2). The magnetic contribution $\rho_{mag}(T)$ to $\rho(T)$ has been obtained by subtracting a phononic contribution, approximated as $\rho_{ph}(T) = 0.1 \mu\Omega cm/K \times T$, from the raw data. Qualitatively, both compounds show the same pressure dependence: Pressure shifts $T_N$ upwards, the signature of the phase transition broadens, and within a small pressure range, the traces of the phase transition vanish. $\rho_{mag}(T)$ exhibits two maxima, reflecting the Kondo scattering from the ground state and excited crystal field levels as often observed for other compounds (indicated by $T_K$ and $T_{max}$, respectively, in Fig. 1 \([8, 16]\). Furthermore, a small and reproducible decrease in $\rho_{mag}(T)$ has been detected at very low temperature (insets of Fig. 1 and Fig. 2).

It occurs in a narrow pressure range in the apparently non-magnetic phase below 110 mK for CePd$_{2}$Ge$_{1.98}$ whereas it was found in CePd$_{2}$Ge$_{2}$ at somewhat lower temperature (70 mK). In each case an increased measuring current density suppressed the anomaly.

These measurements reveal the pressure dependence of $T_N$, as depicted in Fig. 3. As criterion for $T_N$ the intersection of two tangents drawn to $\rho(T)$ has been used. In the case of CePd$_{2}$Ge$_{2}$ both data sets obtained on different samples from the same batch in different pressure cells match perfectly (open and filled squares in Fig. 3). The initial pressure shift $\partial T_N/\partial p = 0.51(1) K/GPa$ is slightly higher than that reported in Ref. \([38]\). The same value is obtained for CePd$_{2.02}$Ge$_{1.98}$ if the values of $T_N$ at ambient pressure and 6 GPa are used. At higher pressures however, both $T_N(p)$-variations are clearly different. In CePd$_{2.02}$Ge$_{1.98}$, $T_N$ does not reach the same absolute value as in the stoichiometric compound and the magnetic order vanishes already at $p_c = 11.0$ GPa, compared to $p_c = 13.8$ GPa for CePd$_{2}$Ge$_{2}$. Thus, the Pd-excess has led to a reduction of $p_c$ by 2.8 GPa.

The extrapolation $T_N \to 0$ (dotted lines in Fig. 3)
FIG. 1: The magnetic part $\rho_{\text{mag}}(T)$ of the electrical resistivity of CePd$_{2.02}$Ge$_{1.98}$ vs temperature, $T$, in a semilogarithmic plot. The antiferromagnetic transition produces a cusp at $T_N$. The scattering of carriers at the ground state and excited crystal field levels produce two maxima at $T_K$ and $T_{\text{max}}$. Inset: An additional phase transition at high pressure might be responsible for the decrease of $\rho_{\text{mag}}(T)$ at about 110 mK.

FIG. 2: Temperature dependence of the magnetic part of the electrical resistivity $\rho_{\text{mag}}(T)$ of CePd$_2$Ge$_2$ in a semilogarithmic plot. The similarity of the high pressure curves to those of CePd$_{2.02}$Ge$_{1.98}$ (cf. Fig. 1) is evident. The small drop in $\rho_{\text{mag}}(T)$ at 70 mK above 14 GPa (inset) might indicate an additional phase transition.

FIG. 3: Pressure dependence of $T_N$ for CePd$_{2+x}$Ge$_{2-x}$ ($x = 0$ and 0.02). The extrapolation $T_N \rightarrow 0$ assumes critical pressures $p_c = 11.0$ GPa ($x = 0.02$) and 13.8 GPa ($x = 0$). Two data sets of $T_N(p)$ for $x = 0$ obtained on different samples match perfectly. The $T_N$ values for $x = 0.02$ obtained by the ac-calorimetry are represented by open circles. Inset: A pronounced variation of the residual resistivity $\rho_0$ with pressure is observed in both compounds.

FIG. 4: Temperature coefficient $\tilde{A}$ obtained from a fit $\rho_{\text{mag}}(T) = \rho_0 + \tilde{A}T^n$ to the data of CePd$_{2+x}$Ge$_{2-x}$ ($x = 0$ and 0.02) below 2 K vs pressure, $p$. $\tilde{A}$ peaks at 11.0 GPa and 13.8 GPa for $x = 0.02$ and $x = 0$, respectively. Inset: The exponent $n$ used to describe $\rho_{\text{mag}}(T)$ at different pressures.
is based on the assumption that the maximum in the $A(p)$ dependence can be taken as critical pressure. The $A$-values have been obtained from fits of $\rho_{\text{mag}}(T) = \rho_0 + A T^n$ to the data below 2 K, with $A$ and $n$ as fitting parameters. The lower bound to the fit is given by the accessible temperature and is about 40 mK. The value for the upper limit is a compromise between an as narrow as possible temperature interval and the reliability of the deduced parameters. The pressure dependence of the temperature coefficient $A$ is qualitatively similar for both compounds and shows a pronounced anomaly which is assumed to be the hallmark of the magnetic/non-magnetic phase transition (see Fig. 4). Both $A(p)$-variations can be mapped on top of each other if a pressure shift of $\Delta \rho_{\text{mag}}(p) = 2.8$ GPa is taken into account. In the magnetically ordered phase the exponent $n > 2$ whereas $n = 2$ is found in the Fermi-liquid regime far above $p_c$ (inset Fig. 4). Exponents smaller than two are observed in a certain pressure range around $p_c$. A minimum $n \approx 1.6$ is attained just above $p_c$ for both compounds. Within a small pressure range around $p_c$, $\rho_{\text{mag}}(T)$ cannot be described by a quadratic temperature dependence even if the temperature interval is 40 mK < $T < 0.6$ K. Similar observations have been reported for CePd$_2$Si$_2$ and other systems, like CeRu$_2$Ge$_2$ and CeCu$_2$Au.

Approaching the verge of magnetism seems also to affect the residual resistivity $\rho_0$. It is very sensitive to small pressure changes and exhibits anomalies around $p_c$ which are qualitatively the same for both compounds (see inset Fig. 6). Just below $p_c$, $\rho_0$ attains a local maximum and passes through a local minimum above $p_c$. Upon further pressure increase $\rho_0$ continuously increases and at 22 GPa reaches several times its ambient pressure value. This variation reflects intrinsic effects since a change of the geometrical factor in such a peculiar manner can be ruled out.

The comparison of the resistivity data presented above reveals that pressure has qualitatively the same effect on both compounds. The main difference is that for CePd$_2$Ge$_2$ less pressure ($\Delta p = 2.7(2)$ GPa) is necessary to achieve the same effect as in CePd$_2$Ge$_2$. Table II summarizes several quantities which show pronounced anomalies in their pressure behavior. From this we infer that not only interatomic distances are important for $J$ since the difference in unit cell volume at ambient pressure cannot explain such a large shift in $p_c$.

| $p_{\text{max}}$ (GPa) | $p_{c}$ | $p_{\text{min}}$ (GPa) | $p_{\text{max}}(1/V_{ac}$T→0) (GPa) | $p_{\text{min}}(1/V_{ac}$T→0) (GPa) | $p_{\text{cal}}$ (GPa) | $\rho_{\text{cal}}$ (GPa) |
|-----------------------|--------|-----------------------|---------------------------------|---------------------------------|--------------------|--------------------|
| 9.7                   | 11.0   | 12.1                  | 12.1                            | 14.6                            | 12.1               | 14.6               |
| 12.3                  | 13.8   | 16.4                  | 16.6                            | 14.6                            | 14.4               | 14.4               |

B. $\text{ac}$-calorimetry on CePd$_{2+2}$Ge$_{1.98}$

Figure 8 shows the inverse of the registered lock-in signal $V_{ac}$ below 10 K at various pressures. The pronounced anomaly in $1/V_{ac}(T)$ for pressures between 6.0 GPa and 10 GPa is caused by the entrance into the antiferromagnetically ordered phase. Taking the temperature of the maximum as $T_N$ yields lower $T_N$-values as those shown in Fig. 3. $T_N$ taken from the midpoint of the 1/$V_{ac}$-anomaly at 6 GPa is the same as that deduced from $\rho(T)$. At higher pressure however, this definition yields larger $T_N$-values than those obtained from $\rho(T)$. The height of the anomaly decreases and it becomes a very broad feature as the system approaches $p_c$. A similar broadening upon approaching $p_c$ has been reported for CeRu$_2$Ge$_2$ and CePd$_2$Si$_2$ examined in pressure cells with solid He as pressure transmitting medium, despite their lower $p_c$-values.

From a general point of view this might be due to inhomogeneous pressure conditions always present regardless the pressure medium and the absolute value of $p_c$. Close to $p_c$ the $T_N(p)$ variation is very strong and a small pressure gradient can easily generate $\Delta T_N = 1$ K. However, other intrinsic effects cannot be excluded to be responsible for a broadening in the vicinity of $p_c$.

A very interesting observation is the pressure dependence of the value of $1/V_{ac}$ taken at the lowest temperature reached in each pressure run (inset Fig. 4). Upon approaching $p_c$ it strongly increases, reaches a maximum just above $p_c$ (which was inferred from the $A(p)$-anomaly), and levels off at high pressure. As was pointed out above, $1/V_{ac}(T) \propto C/T$ at low temperature can be regarded as a direct measure of the electronic correlations. The pronounced pressure dependence of $1/V_{ac}$ shows that the electronic correlations are considerably enhanced as pressure approaches $p_c$ and that the signal originates mainly from the sample.

IV. DISCUSSION

In the following we will first compare the $T_N(V)$-dependence of CePd$_2$Ge$_2$ with that of CePd$_2$Si$_2$. Thereafter, the elaborate discussion of the pressure effects on the CeFe$_{2+x}$Ge$_{2-x}$ compounds ($x = 0$ and 0.02) will reveal a possible explanation of the observed similarities as well as the differences.

The $\rho_{\text{cal}} = 0$ (GPa) for pressures between 4.0 GPa and 5.0 GPa. The pronounced anomaly (see Fig. 4) is a by-product of the entrance into the antiferromagnetically ordered phase. Taking the temperature of the maximum as $T_N$ yields lower $T_N$-values than those obtained from $\rho(T)$. The height of the anomaly decreases and it becomes a very broad feature as the system approaches $p_c$. A similar broadening upon approaching $p_c$ has been reported for CeRu$_2$Ge$_2$ and CePd$_2$Si$_2$ examined in pressure cells with solid He as pressure transmitting medium, despite their lower $p_c$-values. From a general point of view this might be due to inhomogeneous pressure conditions always present regardless the pressure medium and the absolute value of $p_c$. Close to $p_c$ the $T_N(p)$ variation is very strong and a small pressure gradient can easily generate $\Delta T_N = 1$ K. However, other intrinsic effects cannot be excluded to be responsible for a broadening in the vicinity of $p_c$.

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The entrance into the antiferromagnetically ordered state is clearly visible. Inset: The values of $1/V_{ac} \propto C/T$ taken at low temperature show a pronounced peak in the vicinity of $p_c$. The data of CePd$_2$Si$_2$ are taken at low temperature show a pronounced variation, starting at $T_N = 5.1 \text{ K}$, passing through a maximum of about 10 K, and eventually approaching zero. The extrapolation $T_N \rightarrow 0$ yields $V = 171.51 \text{ Å}^3$ which correspond to a pressure of 14.4 GPa, very close to $p_c = 13.8 \text{ GPa}$ deduced from the maximum in $A(p)$. CePd$_2$Si$_2$ reaches this volume at $p_c = 3.9 \text{ GPa}$. This $p_c$-value agrees perfectly with that found in a thorough investigation of the strain enhancement of superconductivity.

The almost perfect match of the two data sets emphasizes the importance of the sample orientation with respect to the direction of the applied force. Figure 6 shows only data from samples with their crystallographic $c$-axis parallel to the applied force exerted to the anvils. The additional uniaxial strain component along the $c$-axis strongly affects the anisotropy of the tetragonal ThCr$_2$Si$_2$ structure. It is known from x-ray absorption studies that a change of the $c$-axis lattice parameter results in a varying chemical bonding strength between the Ce-ions and their ligands. A change in the Ce-valence, however, is thought to influence only the $a$-axis lattice parameter and vice versa. Thus, it seems that the additional uniaxial stress is necessary to change the hybridization in an effective way. In CePd$_2$Si$_2$ it shifts $p_c$ from 2.8 GPa to 3.9 GPa and leads to an increase in the superconducting transition temperature of about 40% compared to values obtained from samples in a configuration where the crystallographic $c$-axis was perpendicular to the external force.

The combined phase diagram clearly demonstrates the analogy between CePd$_2$Ge$_2$ at high pressure and CePd$_2$Si$_2$.
CePd$_2$Si$_2$ at moderate pressures. It can provide an idea about the sudden decrease of \( \rho_{\text{mag}}(T) \) in CePd$_{2.02}$Ge$_{1.98}$ and CePd$_{2}$Ge$_{2}$ at 110 mK and 70 mK, respectively (insets Fig. 1 and Fig. 2). The reduced volume where these anomalies occur is similar to the volume where superconductivity is found in CePd$_2$Si$_2$ (Fig. 3). An interpretation as incipient superconductivity is therefore one possible explanation, especially if the reported properties of CeNi$_{2+y}$Ge$_{2-x}$ and CePd$_2$Si$_2$ are recalled. In the former system \( \rho = 0 \) was only achieved after \( \rho_0 \) had been reduced below 1-2 \( \mu \Omega \text{cm} \). For those samples with higher \( \rho_0 \)-values only traces of superconductivity appeared. Also for the latter compound high-purity samples (\( \rho_0 < 1 \mu \Omega \text{cm} \)) seem to be required for a complete superconducting transition.

The difference in the \( \rho_0 \)-values and the \( A(p) \)-dependence of CePd$_{2.02}$Ge$_{1.98}$ and CePd$_{2}$Ge$_{2}$ can also be understood qualitatively within the Doniach picture. Magnetic order is a cooperative phenomenon involving the alignment of spins over distances which are large compared to the lattice parameter. It is very unlikely that a small change in the Ce-ligand configuration will influence the RKKY interaction and \( J \approx J' \) seems to be justified, with \( J \) and \( J' \) the exchange coupling for \( x = 0 \) and \( x = 0.02 \), respectively. The almost identical \( T_N \)-values at ambient pressure corroborate this assumption. For the Kondo effect however, only the local environment of the Ce-ions is essential and therefore, a small change in its configuration sphere should influence \( T_K \). It seems very likely that the additional Pd in CePd$_{2.02}$Ge$_{1.98}$ occupies Ge-sites and/or interstitial sites and might influence the local environment of the Ce-ions, resulting in \( J' > J \).

Within a certain limit this hypothesis is supported by the different \( \gamma \)-values at ambient pressure (Tab. 1). Furthermore, the x-ray data of CePd$_{2.02}$Ge$_{1.98}$ reveal that the \( c \)-axis lattice parameter is slightly lower, whereas the \( a \)-axis lattice parameter is unchanged within the standard deviation. Thus, the Pd-excess could have caused a stronger hybridization between the \( Jf \) and conduction electrons already at ambient pressure as was argued above. Results of a thorough investigation of the influence of the Ni-excess in Ce$_{1.005}$Ni$_{2+z}$Ge$_{2-z}$ encourage this argumentation. As a function of the Ni-content the \( c \)-axis lattice parameter and \( \rho_0 \) showed a minimum at \( z = 0.02 \) and a complete superconducting transition occurred close to this value at ambient pressure, whereas pressure had to be applied to achieve a superconducting ground state in the stoichiometric compound. With these assumptions \( T_{\text{KKK}}(J) \) will be of comparable strength to \( T_K(J) \) and \( T_K(J') \) at a critical value \( J_c' < J_c \). Therefore, \( p_c \) of CePd$_{2.02}$Ge$_{1.98}$, determined by \( J_c' \), is lower than \( p_c \) of CePd$_{2}$Ge$_{2}$, given by \( J_c \). As a consequence of this consideration a shifted \( A(p) \)-dependence follows, since \( A \propto T_K^{-2} \), as is experimentally found and depicted in Fig. 4.

The Kondo temperature in CePd$_{2}$Ge$_{2}$ at low pressures is small in comparison to the crystal field splitting \( \Delta_1 = 110 \text{ K} \) and \( \Delta_2 = 220 \text{ K} \). Therefore, \( \rho_{\text{mag}}(T) \) shows only one maximum at \( T_{\text{max}} \) at low pressure. Around \( p_c \) however, two maxima at \( T_K \) and \( T_{\text{max}} \) occur, reflecting the Kondo scattering from the ground state and excited state, respectively (Fig. 3 and Fig. 4). The low temperature maximum emerges at a pressure of about 11 GPa and shifts to higher temperatures with increasing pressure as shown in Fig. 5. This might reflect an enhanced screening of the magnetic moments by the conduction electrons and thus point to an increasing role of the Kondo effect. As a consequence, the anomaly at low temperature has to be related to \( T_K \). Both anomalies in \( \rho_{\text{mag}}(T) \) seem to merge in the vicinity of \( p_c \), indicating the entrance into the intermediate valence regime. In this region the crystalline electrical field levels cease to exist as well-defined excitations. In the case of two excited crystal field levels, Hanazawa et al. have introduced a second Kondo temperature \( T_K^h \) at high temperature. It is related to \( T_K \) by \( T_K^h = \sqrt{T_K \Delta_1 \Delta_2} \). Using the assumption that \( \Delta_1 \) and \( \Delta_2 \) decrease under pressure with the same rate as in CePd$_2$Si$_2$ the \( T_K^h \)-values can be calculated as a function of pressure (open symbols in Fig. 5). A good agreement is achieved with the measured values of \( T_{\text{max}} \). Similar considerations can be made for CePd$_{2.02}$Ge$_{1.98}$, resulting in the same phase diagram but shifted by 2.8 GPa to lower pressures.

The analysis of the low temperature behavior of \( \rho_{\text{mag}}(T) \) have revealed almost the same anomalies in \( \rho_0 \), \( A \), and \( n \) for CePd$_{2.02}$Ge$_{1.98}$ and CePd$_{2}$Ge$_{2}$. Of particular interest is the strong pressure dependence of \( \rho_0 \).
(inset Fig. 3). It is an additional example of a pressure dependent residual resistivity scattering in HF compounds already pointed out in Ref. [17]. The anomalies in ρ₀(p) cannot be caused by lattice defects and impurities alone like in conventional metals. The independent-electron approximation (ρ₀ ∝ 1/(k_F^2 l), with k_F the Fermi-wavenumber and l the mean free path) suggests that pressure should affect ρ₀ only weakly since both k_F and l react upon pressure only through the small change of electron density and interatomic distances. In metals with strongly interacting electrons and magnetic order the contributions to ρ₀ are not well understood. So far, a noticeable ρ₀(p)-dependence has been found in several HF systems either in the magnetic phase (CeCu$_2$Au [19] and YbCu$_2$Si$_2$ [14]), close to p_c (CeAl$_3$ [17] or in the paramagnetic phase (CeCu$_2$Ge$_2$ and CeCu$_2$Si$_2$ [7]). Following the suggestion by Miyake and Maebashi [18] quantum critical fluctuations should give rise to an enhanced impurity potential. It leads to an increase of ρ₀ through non-magnetic impurity scattering near a ferromagnetic or antiferromagnetic quantum critical point if many-body corrections of scattering are taken into account. This possibility and the wealth of ρ₀(p) anomalies reported so far might indicate that only a part of ρ₀ is due to static disorder and that the large variation of ρ₀(p) is an intrinsic property of a weakly disordered Kondo lattice [13].

The deviation from a FL behavior around p_c is an established fact and can be understood in the framework of spin fluctuation theory [19, 50]. For spin fluctuations with 3D character ρ(T) = ρ₀ + AT^n, with n = 1.5, is expected. The minimum values of n depicted in Fig. 1 are close to this value. It is considerably different from a linear temperature dependence which is expected for a distribution of Kondo temperatures [51]. Therefore, Kondo disorder seems to be negligible.

The ac-calorimetry data revealed a pronounced variation of the ac-signal recorded below 1 K. It was argued above that 1/V_{ac} can be taken as the linear coefficient of the specific heat, C/T = γ. Its pressure dependence is not strong enough to follow the A(p)-dependence according to the empirical Kadowaki-Woods relation [52]. Especially at pressures above 15 GPa, the low temperature value of 1/V_{ac} decreases less than expected from A(p) [30]. A possible reason for this deviation might be the unknown thermal properties of the pressure transmitting medium (and perhaps also of the sample) at high pressure. They have changed significantly, which was only accounted for by adjusting the measuring frequency. A step towards a quantitative measure of C_p at these conditions would be to achieve a control of the supplied heating power and the thermal contact between sample and pressure transmitting medium. Nevertheless, the strong pressure dependence of 1/V_{ac} at low temperature is reminiscent to A(p) and is a motivation for further studies.

V. CONCLUSION

We reported results of a combined electrical resistivity, ρ(T), and ac-calorimetry, C(T), investigation of the antiferromagnetically ordered CePd$_2$Ge$_1$$_9$$_8$ (T_N = 5.16 K) and ρ(T) measurements of CePd$_2$Ge$_2$ (T_N = 5.12 K) for pressures up to 22 GPa. Both measuring techniques have been assembled in one Bridgman-type of high pressure cell. The particular sample arrangement guarantees similar pressure conditions essential for a comparison of the pressure induced effects. The ac-calorimetry and ρ(T)-data have been obtained from the same sample which is important to demonstrate the feasibility of the ac-technique at these extreme conditions. Both methods reveal a suppression of magnetic order at a critical pressure p_c = 11.0 GPa and p_c = 13.8 GPa for CePd$_2$Ge$_1$$_9$$_8$ and CePd$_2$Ge$_2$, respectively. The inverse of the ac-signal 1/V_{ac} ∝ C/T recorded at the lowest temperature exhibits an anomaly in the vicinity of p_c, reminiscent to A(p), the temperature coefficient of ρ(T). Although the pressure dependence of 1/V_{ac} is not strong enough to follow the entire A(p) dependence according to the Kadowaki-Woods relation it is evident that the ac-signal mainly represents the sample properties. These observations demonstrate the sensitivity of the ac-calorimetry to electronic correlations despite the small sample mass (some µg). From the combined (T, V) phase diagram of CePd$_2$Ge$_2$ and CePd$_2$Si$_2$ it was concluded that interatomic distances play a crucial role for the hybridization between the 4f and conduction electrons, i.e., for the exchange coupling J, in the stoichiometric compound. In order to explain the large difference in the p_c-values it was argued that the Ce-coordination sphere in CePd$_2$Ge$_2$ has changed due to the Pd-excess in respect to CePd$_2$Si$_2$. This affects the Kondo temperature, T_K, and therefore T_K will be comparable to the RKKY interaction at a lower critical value of J for CePd$_2$Ge$_1$$_9$$_8$. With this assumption the shifted A(p)-variations have also been explained. The deviation of ρ(T) from a Fermi-liquid behavior in the vicinity of p_c can be ascribed to 3D spin fluctuations. The strong variation of the residual resistivity ρ₀ with pressure around p_c might indicate that only a part of ρ₀ is due to static disorder. As a consequence, the assumption of a powerlaw for ρ(T) will be a subject of further careful investigations, especially at very low temperatures.

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