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2002 J. Phys.: Condens. Matter 14 10683

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# Alternating current calorimetry at very high pressure and low temperature

H Wilhelm<sup>1,2</sup> and D Jaccard<sup>1</sup>

<sup>1</sup> DPMC, University of Geneva, Quai Ernest-Ansermet 24, 1211 Geneva 4, Switzerland

<sup>2</sup> Max-Planck-Institute for Chemical Physics of Solids, Nöthnitzer-Str. 40, 01187 Dresden, Germany

Received 11 June 2002

Published 25 October 2002

Online at [stacks.iop.org/JPhysCM/14/10683](http://stacks.iop.org/JPhysCM/14/10683)

## Abstract

The specific heat of CePd<sub>2.02</sub>Ge<sub>1.98</sub> has been measured with an ac calorimetric technique up to 22 GPa for temperatures in the range 0.3 K <  $T$  < 10 K. A thermocouple allowed the temperature oscillations to be read when an ac heating current was sent through the sample. The inverse of the thermovoltage  $V_{ac}$  recorded at low temperature exhibits a pronounced anomaly as a function of pressure. It is shown that  $1/V_{ac}$  extrapolated to zero temperature is a measure of the Sommerfeld coefficient  $\gamma$ .

## 1. Introduction

Specific heat ( $C_p$ ) is one of the important quantities that solid-state research is interested in. Its temperature dependence can deliver hints about microscopic energy scales and provides a powerful tool for identifying phase transitions. In this respect  $C_p(T)$  measurements are indispensable not only for experimentalists. This has triggered the development of different and very sophisticated technical realizations for obtaining  $C_p(T)$  from the millikelvin range up to very high temperature. The available methods can be divided into two categories. Adiabatic techniques make up one category and are considered as the most accurate ways to estimate the absolute value of  $C_p(T)$ . They require sample masses of several grams and the subtraction of the contributions of the addenda, i.e. the specific heat of the sample holder and thermometer. Among the non-adiabatic (or dynamic) methods making up the other category, ac calorimetry [1] is a suitable technique for investigating samples with masses well below 1 mg. Very high sensitivity can be achieved, despite these small masses. However, the absolute accuracy which can be achieved is less than for the adiabatic techniques.

Adiabatic techniques are used to detect pressure-induced phase transitions or to investigate the evolution of electronic properties as the unit-cell volume is reduced. The sample masses needed demand large-volume pressure cells, such as a piston–cylinder cell [2]. With this technique the accessible pressure range is, however, limited to about 2 GPa. Very often it would be desirable for the pressure range to be extended. In this case an anvil type of pressure cell is the only alternative. For such a high-pressure tool, much smaller sample volumes are

required, which make adiabatic measurement a hopeless venture. Thus, ac calorimetry is an ideal method to use for pressures beyond 2 GPa.

In a recent study it was shown that  $C_p(T)$  can be investigated in a Bridgman-type high-pressure cell up to 10 GPa and for temperatures in the range  $1.5 \text{ K} < T < 12 \text{ K}$  [3]. In this experiment the sample was embedded in a soft mineral and an ac current was supplied to a heater close to the sample. These results have been confirmed by an independent study using a diamond anvil cell with He as the pressure-transmitting medium and laser heating [4]. Motivated by these results, we implemented the ac calorimetry in a Bridgman-type high-pressure cell capable of reaching 25 GPa and temperatures of the order of 30 mK [5, 6]. Since the electrical connections for the specific heat set-up are very similar to those of an electrical resistivity ( $\rho(T)$ ) measurement, this opens the possibility of recording both  $\rho(T)$  and  $C_p(T)$  for the *same* sample.

We have chosen  $\text{CePd}_{2.02}\text{Ge}_{1.98}$  because in its stoichiometric form it is the Ge-doped counterpart of the antiferromagnetically ordered heavy-fermion compound  $\text{CePd}_2\text{Si}_2$  ( $T_N \approx 10 \text{ K}$ ). The latter has been shown to become superconducting close to the critical pressure  $p_c$  of 2.7 GPa, where the magnetic order is suppressed [7–9]. The replacement of Si by Ge reduces the electron correlations and leads to a slightly enhanced Sommerfeld coefficient ( $\gamma = 8 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ) as a result of the very slight f character of the conduction electrons [10]. As a consequence, the magnetic ordering temperature is reduced ( $T_N = 5.1 \text{ K}$  [10]). Applying pressure to  $\text{CePd}_2\text{Ge}_2$ , which has a larger unit-cell volume than  $\text{CePd}_2\text{Si}_2$ , should increase the electronic correlations. The aim of the work presented here was to study the influence of a slight Pd excess on the ordering temperature ( $T_N = 5.05(5) \text{ K}$  [11]) and to extract the electronic contribution to the specific heat of  $\text{CePd}_{2.02}\text{Ge}_{1.98}$ . More details about this experiment as well as the results obtained for  $\text{CePd}_2\text{Ge}_2$  are presented in [11].

## 2. Experimental details

The sample of  $\text{CePd}_{2.02}\text{Ge}_{1.98}$  was prepared by melting amounts of Ce(4N), Pd(5N), and Ge(6N) according to the required composition in an induction furnace under an Ar(6N) atmosphere. Part of the polycrystalline ingot was analysed by means of x-ray powder diffraction and yielded as the lattice parameter for the  $\text{ThCr}_2\text{Si}_2$  structure ( $I4/mmm$ )  $a = 4.3399(7) \text{ \AA}$  and  $c = 10.0343(19) \text{ \AA}$  ( $V = 189.00(7) \text{ \AA}^3$ ). The best resistivity ratios ( $\rho(295 \text{ K})/\rho(4.2 \text{ K})$ ) have been obtained for samples annealed for two days at 1420 K. The sample composition corresponds to the initial masses. Mass loss during melting and annealing was negligible. A sample with a cross-section  $22 \times 48 \text{ \mu m}^2$  was prepared for the pressure experiment. The distance between the voltage leads was  $272 \text{ \mu m}$  before pressurization. The high-pressure cell used in this experiment is derived on the basis of the Bridgman technique [5, 6]. As the pressure gauge, the pressure dependence of the superconducting transition temperature of Pb was used.

For the specific heat experiment the sample was thermally excited by an ac current passed through the sample itself. The amplitude of the temperature oscillations  $T_{ac}$  was measured with a AuFe/Au thermocouple attached to the sample. The thermovoltage  $V_{ac}$  of the AuFe/Au thermocouple arises from the temperature difference between the sample (at  $T_0 + \Delta T$ ) and the edge of the sample chamber (at  $T_0$ ) [5]. Assuming that the heat capacity of the thermometer can be neglected and that the coupling between the sample and thermometer is ideal,  $T_{ac}$  is only related to the mean heat power  $P$ , the thermal conductance between the sample and bath  $\Lambda$ , the specific heat  $C$  of the sample, and the working frequency  $\omega$ :

$$T_{ac} = \frac{P}{\Lambda + i\omega C} \propto \frac{P}{\omega C}$$

with  $i^2 = -1$ . The right-hand side of this equation is valid if the measurement is made above the cut-off frequency:  $\omega > \omega_{cut} = \Lambda/C$ . The inverse of the recorded lock-in voltage  $V_{ac}$  is proportional to  $C/T$ , since  $S(T) \propto T$  is a fairly good assumption at low temperature ( $T \leq 1$  K). Thus, the value of  $1/V_{ac}$  recorded at temperatures below 1 K is proportional to the Sommerfeld coefficient  $\gamma$ . Above 1 K the  $S(T)$  dependence is certainly different from that at lower temperatures and  $1/V_{ac}$  has to be interpreted with caution. However, anomalies in  $1/V_{ac}$  are related to the sample and can be regarded as fingerprints of a phase transition. In the present set-up this could be checked independently by  $\rho(T)$  measurements on the *same* sample.

The pressure dependence of the absolute thermopower  $S(T)$  of AuFe can be determined if the sample is used as a thermometer. Here, we only determined  $S(T)$  at 4.2 and 1.0 K in order to have a rough estimate of the influence of pressure on  $S(T)$ . In a first step,  $\rho(T)$  for the sample was determined. Then the sample's resistance was recorded as a function of the (heating) current while the pressure cell was kept at a fixed temperature. In a second step, the thermovoltage produced by the same heating current applied to the sample was registered. The thermovoltage induced for a given current was related to a temperature difference with respect to the pressure cell's temperature, using the  $\rho(T)$  dependence of the sample. This finally yielded the absolute thermopower of AuFe. The values obtained for 4.2 and 1.0 K at 12 GPa are about 20% smaller than the values at ambient pressure. These rather small changes show that, apart from a systematic error due to the change in  $S(T)$ , the interpretation of the results reported in this work is not affected qualitatively. Nevertheless, a systematic investigation of the pressure-induced changes in  $S_{AuFe/Au}(T)$  up to very high pressure is necessary if we wish to make quantitative statements.

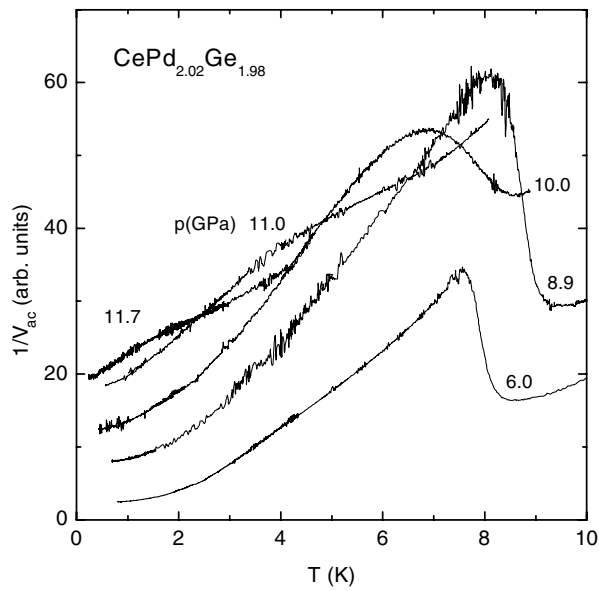
The entire experiment depends crucially on the mechanical stability of the electrical circuit, especially on the location of the thermocouple at the sample. The sample chamber and the position of the leads were carefully re-examined after pressure release. The overall shape of the pressure cell as well as its initial diameter were almost unchanged and the distance between the voltage leads had increased by less than 5%. This confirms that the determination of the absolute value of  $\rho(T)$  is reliable within this uncertainty and that the specific heat can be measured qualitatively at high pressures.

### 3. Results and discussion

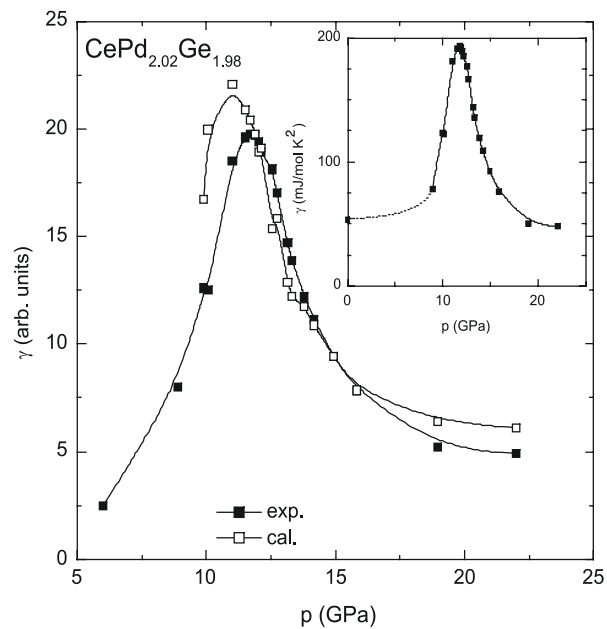
Figure 1 shows the inverse of the registered lock-in signal  $V_{ac}$  below 10 K at various pressures. A pronounced anomaly is observed between 6.0 and 10 GPa. It is caused by the entry into the antiferromagnetically ordered phase. The temperature where the maximum of the pronounced anomaly occurred was chosen as  $T_N$ . The height of the anomaly decreases and its position shifts towards zero temperature as the system approaches the critical pressure. An independent  $\rho(T)$  measurement showed that at almost the same temperature there was a drop or a cusp in the resistivity data [11].

The most intriguing finding of this investigation is the variation of  $1/V_{ac}$  below 0.5 K. Upon pressure increase, it increases and reaches a maximum at 11.7 GPa. At higher pressures,  $1/V_{ac}$  starts to decrease (not shown; for more details see [11]). As was pointed out above,  $1/V_{ac}(T)$  extrapolated to  $T = 0$  can be regarded as a direct measure of the Sommerfeld coefficient  $\gamma$ . Thus, this pressure dependence reflects the evolution of  $\gamma$  with pressure. The pronounced maximum in  $\gamma(p)$  visible in figure 2 is centred at 11.7 GPa—almost at the pressure deduced to be the critical pressure from the  $\rho(T)$  data [11]. This shows that the electronic correlations are enhanced considerably close to the critical pressure.

Electrical resistivity data support the assumption that  $1/V_{ac}$  is a measure of  $\gamma$ . In the main part of figure 2, the calculated  $\gamma(p)$  variation is also presented. It is obtained from the Fermi-



**Figure 1.** The temperature dependence of the inverse lock-in voltage  $V_{ac}$  measured for  $\text{CePd}_{2.02}\text{Ge}_{1.98}$  at low temperature. The signal was measured with frequencies between 750 Hz and 3 kHz. The anomaly due to the antiferromagnetic phase transition is clearly visible between 6 and 10 GPa. Closer to the critical pressure, the magnetic transition is present as a broad feature.



**Figure 2.** Experimental and calculated values of the Sommerfeld coefficient  $\gamma$  versus pressure. The empirical Kadowaki–Woods relation was used to calculate  $\gamma$  (open symbols) from the Fermi-liquid coefficient  $A(p)$  obtained from  $\rho(T)$  [11]. The inset shows  $\gamma$  in absolute units.

liquid coefficient  $A$  of the electrical resistivity using the empirical Kadowaki–Woods relation  $\gamma^2 = 10^5 A$  [12]. For this comparison we used  $A$ -values obtained from a fit of a quadratic temperature dependence to  $\rho(T)$  below 0.6 K and made the assumption that  $\gamma^{cal} = b+c\gamma$ . This shows that in addition to a scaling factor ( $b = 5.75$ ), a constant offset ( $c = 81.7 \times 10^{-3}$  arbitrary units) has to be taken into account. The adjustment of the calculated to the experimental data was made at 13.8 and 14.9 GPa. The values extracted from this calculation show a good agreement with the experimental data above  $p_c$  and provide additional support for the assumption that  $1/V_{ac}$  at low temperature is a measure of the electronic contribution to  $C_p$ .

One can even go one step further and calculate the absolute value of  $\gamma$  (see the inset of figure 2). For this consideration we adjusted  $\gamma^{exp}$  at 11.7 GPa to the corresponding  $A$ -values using the Kadowaki–Woods relation. This yields  $\gamma \approx 200 \text{ mJ mol}^{-1} \text{ K}^{-2}$  around  $p_c$  and shows that the correlations present at ambient pressure ( $\gamma = 101 \text{ mJ mol}^{-1} \text{ K}^{-2}$  [11]) are considerably enhanced at  $p_c$ .

#### 4. Conclusions

We have reported specific heat measurements on the magnetically ordered compound  $\text{CePd}_{2.02}\text{Ge}_{1.98}$  made using an ac calorimetric technique for pressures up to 22 GPa and temperatures as low as 0.3 K. The results show that a semi-qualitative measurement of the specific heat under these extreme conditions is feasible and that the main contribution to  $1/V_{ac}$  results from the sample's specific heat. A quantitative analysis, however, is for the time being not possible, since a calibration of the thermocouple at high pressure has to be done and the total heat transfer to the sample is unknown. The consistency of the measurement could only be tested on the basis of general arguments, such as entropy conservation, or by comparison with other experimental results. This experiment has shown that the sensitivity of the ac calorimetric technique is high enough for following the evolution of electronic interactions with pressure, and not only in strongly correlated systems.

#### Acknowledgments

We thank Y Wang and A Junod for helpful discussions about ac calorimetry and N Caroca-Canales at the MPI CPfS for performing the x-ray analysis.

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