Single crystal growth of CeNi2Ge2 using the floating zone technique

C. Bergmann, H. S. Jeevan, M. Schubert, C. Geibel, Philipp Gegenwart

Angaben zur Veröffentlichung / Publication details:

Bergmann, C., H. S. Jeevan, M. Schubert, C. Geibel, and Philipp Gegenwart. 2010. "Single crystal growth of CeNi2Ge2 using the floating zone technique." *physica status solidi (b)* 247 (3): 694–96. https://doi.org/10.1002/pssb.200983060.

Single crystal growth of $CeNi_2Ge_2$ using the floating zone technique

C. Bergmann[1], H. S. Jeevan[1], M. Schubert[1], C. Geibel[2], and P. Gegenwart[*,1]

[1] I. Physikalisches Institut, Georg-August-Universität Göttingen, 37077 Göttingen, Germany
[2] Max-Planck Institute for Chemical Physics of Solids, D-01187 Dresden, Germany

[*] Corresponding author: e-mail pgegenw@gwdg.de, Phone: +49 551 39 7607, Fax: +49 551 39 19546

In order to investigate the low-temperature electronic properties of the heavy-fermion metal $CeNi_2Ge_2$, single crystals were grown using the floating zone technique. Previous investigations on polycrystals of $CeNi_2Ge_2$ have revealed that the low-temperature properties, i.e., non-Fermi liquid (NFL) behavior and incipient superconductivity, are strongly sample dependent, possibly due to a slight variation of the Ni and Ge content. We prepared polycrystalline feed rods of slightly off-stoichiometric composition by induction or arc-melting methods and grew single crystals using a four-mirror optical furnace under high-purity argon atmosphere. As a result, large single crystals of few centimeter size have been obtained. Annealed pieces were investigated by measurements of the temperature dependence of the electrical resistivity $\rho(T)$. A clear correlation between the starting composition and the obtained resistivity ratio (RR_{2K}) was found with the highest ratio for a nominal starting composition of $Ce_{0.98}Ni_{2.025}Ge_{1.975}$ ($RR_{2K} = 29$). The temperature dependence of the electrical resistivity is similar as reported previously and displays NFL behavior below 1 K.

1 Introduction Quantum criticality in heavy-fermion (HF) metals has attracted considerable interest due to the observation of pronounced non-Fermi liquid (NFL) effects like a divergence of the quasiparticle (QP) mass or QP–QP scattering cross-section in the approach of the quantum critical point (QCP) [1, 2]. While there is an increasing number of NFL systems studied by low-temperature transport and thermodynamic experiments, for much less systems the low-energy magnetic fluctuations and the Fermi surface topology close to the QCP have been investigated by inelastic neutron scattering (INS) and de Haas-van Alphen experiments, respectively. In particular the former experiments often require large single crystals, whereas for the latter a very high quality, i.e., a very low residual resistivity ρ_0, is necessary.

Here we focus on the HF metal $CeNi_2Ge_2$, crystallizing in the $ThCr_2Si_2$ structure, which displays NFL behavior [3]. This system has a Kondo temperature of about 30 K and remains paramagnetic down to lowest temperatures with an electronic specific heat coefficient of about 350 mJ/mol K^2 at 0.1 K [4]. Studies on single crystals have revealed a weak magnetic anisotropy with the easy axis along the c-axis. Along this direction, the susceptibility displays a broad maximum around 28 K and the low-temperature magnetization reveals a metamagnetic-like transition at 42 T [5]. Antiferromagnetic (AF) correlations with characteristic energy of about 0.6 meV have been found in INS experiments [6] and the closeness to an AF QCP is proven by the inducement of long-range AF ordering by small Pd- or Cu-doping on the Ni site [7, 8]. Systems close to QCPs are expected to depend very sensitively on small perturbations. Indeed a substantial sample dependence has been found below 1 K for $CeNi_2Ge_2$, with diverging or saturating specific heat coefficients and different resistivity exponents ε in $\rho(T) - \rho_0 \propto T^{\varepsilon}$ ranging between 1.2 and 2 [3–5, 9–11]. The onset of superconductivity has been found in electrical resistivity, without prove for its bulk nature. Previous systematic investigations on slightly off-stoichiometric $Ce_{1+x}Ni_{2+y}Ge_{2-y}$ polycrystals have revealed a strong sensitivity of the low-temperature electrical resistivity [12], specific heat coefficient [13], and thermal expansion [14] on the Ni:Ge ratio. The lowest residual resistivity of 0.17 $\mu\Omega$ cm has been obtained for $y = 0.025$. Because of the particularities of the Ce–Ni–Ge ternary chemical phase Diagram [15], $y = 0$ polycrystals have a Ge-rich 122 phase and the stoichiometric 122 phase is expected at slight Ni

excess [13], which also leads to a small increase of the hybridization, similar as Cu-excess in $CeCu_2Si_2$ [12].

In this paper, we report the successful growth of large single crystals of $CeNi_2Ge_2$ using the crucible free floating zone technique from slightly off-stoichiometric polycrystalline feed rods and report their low-temperature electrical resistivity behavior.

2 Experimental details Arc-melted polycrystalline $CeNi_2Ge_2$ was prepared from the nearly stoichiometric composition of the starting materials (Ce4*N*, Ni4*N*, Ge5*N*). Several polycrystalline buttons with fine tuning of the Ce:Ni ratio were prepared, and casted into a cylindrical form as a feed rod with dimensions of about 4–5 mm diameter and 50–60 mm length using induction or arc melting facilities. The mirror furnace (high-temperature optical floating zone furnace from Crystal Systems Corp.) has four 90° rotated lamps (each 0.5 kW) in a plane, resulting in a relatively homogeneous transmission of the power. We start the growth with two rods as upper and lower shaft in vertical arrangement. The rods are in a 5 bar Ar pressure with flow rate of about 1 L/h. The 5.0 Ar is additionally cleaned with a passive purifier to avoid further oxidation. After we got a melt at the end of one shaft, they are connected to each other, and the lower shaft is moved with 8 mm/h downwards for 2 mm, so that the melt is stretched and forms a neck (Fig. 1a). Such a necking process was adopted to make a single grain at the beginning of growth. While keeping the speed of the lower shaft constant, we start the movement of the upper one with 5 mm/h. Such a difference between the speed of the rods is the best for a stable liquid. The obtained single crystals were oriented and cut along their crystallographic axis. The electrical resistivity was determined with the standard four terminal ac-technique. For measurements down to 50 mK a ^{3}He–^{4}He dilution refrigerator has been utilized.

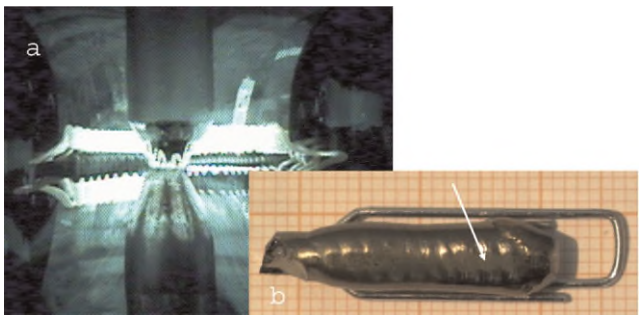

Figure 1 (online color at: www.pss-b.com) Photographs of the stretched melt at the beginning of the single crystal growth (a) and grown single crystal CB0015 with the neck on the left side and surface (indicated by arrow) which is perpendicular to the *c*-axis (b).

3 Results and discussion The X-ray diffraction confirms the formation of $CeNi_2Ge_2$. Energy dispersive X-ray (EDX) analysis reveals a composition of single crystals which is close to 1:2:2 and without detectable variation of the stoichiometry throughout the single crystals. Figure 1a, taken during the crystal growth of $CeNi_2Ge_2$ from feeding rods, illustrates the necking of melt in order to get a single grain. Using this method we succeeded to grow single crystals with a length of 20–30 mm and a diameter of 5–6 mm, as shown in Fig. 1b. The surface indicated by the arrow is aligned perpendicular to the *c*-direction, as determined by Laue backscattering.

Table 1 Starting composition, orientation annealing properties, resistivity ratios, and lattice parameters of studied single crystals.

identifier	composition	orientation	annealing	$RR_{4.2K}$	RR_{2K}	*a* (Å)	*c* (Å)
CB0001.1	$CeNi_2Ge_2$	–	–	7.7	–	–	–
CB0001.2	$CeNi_{2.02}Ge_2$	–	–	9.0	–	–	–
CB0001.2	$CeNi_{2.02}Ge_2$	–	100 h, 800 °C	13.3	19.5	–	–
CB0005.1	$Ce_{0.98}Ni_{2.025}Ge_{1.975}$	–	–	8.4	10.1	–	–
CB0005.1	$Ce_{0.98}Ni_{2.025}Ge_{1.975}$	–	100 h, 800 °C	16.8	24.6	–	–
CB0005.2	$Ce_{0.98}Ni_{2.025}Ge_{1.975}$	–	–	8.0	9.3	–	–
CB0005.2	$Ce_{0.98}Ni_{2.025}Ge_{1.975}$	–	100 h, 800 °C	16.8	25.9	–	–
CB0005.3	$Ce_{0.98}Ni_{2.025}Ge_{1.975}$	–	100 h, 800 °C	19.4	29.1	4.154 (2)	9.851 (3)
CB0005.4	$Ce_{0.98}Ni_{2.025}Ge_{1.975}$	–	100 h, 800 °C	17.0	25.0	–	–
CB0012	$Ce_{1.02}Ni_{2.025}Ge_{1.975}$	–	100 h, 800 °C	14.8	21.0	4.156 (2)	9.859 (3)
CB0015.1	$CeNi_{2.05}Ge_2$	$\|\|a$	–	8.8	10.1	–	–
CB0015.1	$CeNi_{2.05}Ge_2$	$\|\|a$	168 h, 900 °C	8.8	15.2	–	–
CB0015.3	$CeNi_{2.05}Ge_2$	$\|\|c$	–	7.4	8.7	–	–
CB0015.3	$CeNi_{2.05}Ge_2$	$\|\|c$	168 h, 900 °C	8.5	–	–	–
CB0016	$Ce_{1.02}Ni_{2.025}Ge_{1.975}$	–	–	8.7	–	–	–
CB0019	$Ce_{0.98}Ni_{2.025}Ge_{1.975}$	–	–	7.0	–	–	–
CB0020	$Ce_{0.98}Ni_{2.05}Ge_{1.975}$	–	–	7.1	–	–	–
CB0020.1	$Ce_{0.98}Ni_{2.05}Ge_{1.975}$	–	14 days, 1000 °C	9.2	11.73	4.153 (3)	9.862 (7)
CB0020.2	$Ce_{0.98}Ni_{2.05}Ge_{1.975}$	–	14 days, 1000 °C	10.13	12.82	–	–
CB0021	$CeNi_{2.025}Ge_{1.975}$	–	–	10.0	–	–	–
CB0021	$CeNi_{2.025}Ge_{1.975}$	–	100 h, 950 °C	17.1	–	4.151 (2)	9.845

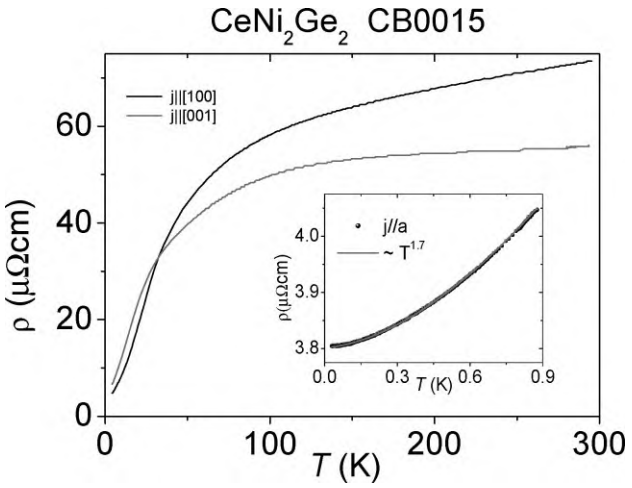

Figure 2 (online color at: www.pss-b.com) Temperature dependence of the electrical resistivity of $CeNi_2Ge_2$ single crystal CB0015 for current along the *c*- and *a*-axis. The inset displays low-temperature data along the *c*-axis. The line indicates a power-law fit (see text).

Table 1 gives an overview on the parameters used to grow single crystals with slightly differing starting compositions for the feed rods together with the values of the resistivity ratio ($RR_{4.2K}$) at 4.2 K and at 2 K (RR_{2K}). For unannealed crystals no significant differences in the RR_{2K} values are observed. Since the floating-zone technique is a fast growth method, RR_{2K} could be strongly increased by annealing. After annealing, the highest obtained RR_{2K} is 29 at 2 K, corresponding to $\rho_0 \sim 1\,\mu\Omega\,\mathrm{cm}$, which is still larger than $0.17\,\mu\Omega\,\mathrm{cm}$ for the best polycrystal studied in [12]. Similar as found for polycrystals, the *c*-axis parameter is smallest for the best crystals.

In order to study the anisotropy of the electrical resistivity, we have oriented the crystal CB0015 by Laue pattern and cut two oriented pieces, which have been measured along the *c*- and *a*-axis in the temperature range from 300 down to 4.2 K. As shown in Fig. 2 a clear anisotropy is found with room temperature values of 50 and 75 $\mu\Omega\,\mathrm{cm}$ along and perpendicular to the *c*-axis, in agreement with previous reports [5]. The low-temperature resistivity for $j \parallel a$ is best fitted by a power-law dependence $\rho(T) = \rho_0 + AT^{\varepsilon}$ with $\rho_0 = 3.8\,\mu\Omega\,\mathrm{cm}$, $A = 0.31\,\mu\Omega\,\mathrm{cm\,K}^{-\varepsilon}$ and $\varepsilon = 1.69$ (inset Fig. 2). This result indicates NFL behavior, although the exponent is slightly larger than in previous studies [3, 9, 10]. It is well known for $CeNi_2Ge_2$, that the exponent is sample dependent and more detailed studies on single crystals with better RR_{2K} are desired.

To conclude, we have successfully grown large single crystals of $CeNi_2Ge_2$ with RR_{2K} values up to 29 at 2 K. In order to further improve the sample quality, fine tuning of the growth parameters is required.

Acknowledgements We thank Ralf Weise for his help during the preparation of the polycrystalline rods with the induction furnace and K. Winzer for his useful advise in crystal orientation, cutting, and resistivity measurements. This work was supported by the DFG research unit 960 "Quantum phase transitions."

References

[1] H. v. Löhneysen, A. Rosch, M. Vojta, and P. Wölfle, Rev. Mod. Phys. **79**, 1015 (2007).
[2] P. Gegenwart, Q. Si, and F. Steglich, Nature Phys. **4**, 186 (2008).
[3] P. Gegenwart, F. Kromer, M. Lang, G. Sparn, C. Geibel, and F. Steglich, Phys. Rev. Lett. **82**, 1293 (1999).
[4] G. Knopp, A. Loidl, R. Caspary, U. Gottwick, C. D. Bredl, H. Spille, F. Steglich, and A. P. Murani, J. Magn. Magn. Mater. **74**, 341 (1988).
[5] T. Fukuhara, K. Maezawa, H. Ohkuni, J. Sakurai, H. Sato, H. Azuma, K. Sugiyama, Y. Onuki, and K. Kindo, J. Phys. Soc. Jpn. **65**, 1559 (1996).
[6] H. Kadowaki, B. Fak, T. Fukuhara, K. Maezawa, N. Kakajima, M. A. Adams, S. Raymond, and J. Flouquet, Phys. Rev. B **68**, 140402(R) (2003).
[7] F. Steglich, P. Gegenwart, C. Geibel, R. Helfrich, P. Hellmann, M. Lang, A. Link, R. Modler, G. Sparn, N. Büttgen, and A. Loidl, Physica B **223–224**, 1 (1996).
[8] G. Knebel, M. Brando, J. Hemberger, M. Nicklas, W. Trinkl, and A. Loidl, Phys. Rev. B **59**, 12390 (1999).
[9] S. Koerner, E.-W. Scheidt, T. Schreiner, K. Heuser, and G. R. Stewart, J. Low Temp. Phys. **119**, 147 (2000).
[10] F. M. Grosche, P. Agerwal, S. R. Julian, N. J. Wilson, R. K. W. Haselwimmer, S. J. S. Lister, N. D. Mathur, F. V. Carter, S. S. Saxena, and G. G. Lonzarich, J. Phys.: Condens. Matter **12**, L533 (2000).
[11] R. Küchler, N. Oeschler, P. Gegenwart, T. Cichorek, K. Neumaier, O. Tegus, C. Geibel, J. A. Mydosh, F. Steglich, L. Zhu, and Q. Si, Phys. Rev. Lett. **91**, 066405 (2003).
[12] P. Gegenwart, P. Hinze, C. Geibel, M. Lang, and F. Steglich, Physica B **281–283**, 5 (2000).
[13] T. Cichorek, C. Geibel, N. Carocca-Canales, T. Lühmann, P. Gegenwart, and F. Steglich, Acta Phys. Pol. B **34**, 371 (2003).
[14] R. Küchler, P. Gegenwart, F. Weickert, N. Oeschler, T. Cichorek, M. Nicklas, N. Carocca-Canales, C. Geibel, and F. Steglich, Physica B **378–380**, 36 (2006).
[15] P. Salamakha, M. Konyk, O. Sologub, and O. Bodak, J. Alloys Compd. **236**, 206 (1996).