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## Superconductivity, upper critical field and normal state resistivity in CeNi<sub>2</sub>Ge<sub>2</sub> under pressure

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**Abstract.** We have performed transport and susceptibility measurements on single-crystal CeNi<sub>2</sub>Ge<sub>2</sub> under high pressure and magnetic field. Under pressure a 30% decrease of the resistivity is found below 300 mK which could be due to the onset of superconductivity. Assuming this we have established the phase diagram of the superconducting phase under pressure and magnetic field. The analysis of  $H_{c2}$  and the slope at  $T_c$  in comparison to a previously published report of superconductivity at ambient pressure might indicate a change in the order parameter with pressure. The normal state resistivity at ambient pressure does not show a quadratic temperature dependence. Under pressure a quadratic dependence is found and we show that the parameters of the resistivity and the susceptibility obey a simple scaling law. This scaling breaks down however when approaching the magnetic instability.

### 1. Introduction

The heavy fermion compounds are often characterized by their proximity to a quantum critical point (QCP) where the magnetic ordering temperature goes to zero and the classical Fermi-liquid description of a normal metal should break down. Among the known stoichiometric compounds, the paramagnetic ground state of CeNi<sub>2</sub>Ge<sub>2</sub> is probably the closest to the QCP at ambient pressure. In other compounds where the ordering temperature has been tuned to zero by the application of pressure, superconductivity has been found close to the QCP, and there are convincing arguments that this could be promoted by the low energy magnetic excitations which exist at this point [1]. In CeNi<sub>2</sub>Ge<sub>2</sub> at ambient pressure possible traces of superconductivity have been observed [2, 3] and very recently a complete loss of resistance in one sample has been reported [4] which implies the existence of a superconducting phase with  $T_c = 0.2$  K and an upper critical field of about 0.6 T. Nevertheless most samples of CeNi<sub>2</sub>Ge<sub>2</sub> do not show indications of bulk superconductivity. This could be due to insufficient sample quality as, if the superconductivity is of an unconventional type, it should be extremely sensitive to impurities, even of non-magnetic character. On the other hand experiments under high pressure above 15 kbar have shown the appearance of superconductivity with an onset critical temperature of about 150 mK, increasing to about 400 mK at higher pressure [4, 5].

This superconducting phase, although still somewhat sample dependent, seems more reliably an intrinsic property.

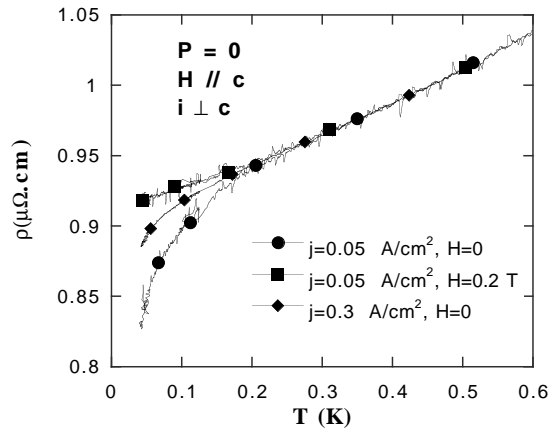
The temperature dependence of the normal state resistivity has not been fully elucidated in CeNi<sub>2</sub>Ge<sub>2</sub> because of its subtle behaviour due to the proximity to the QCP. According to the self-consistent renormalized spin fluctuation theory [6], when a three-dimensional electron system is just at the QCP with antiferromagnetic interaction, the leading term in the resistivity is  $T^{3/2}$ . Except for this critical situation, a well defined  $T^2$  behaviour should appear below some characteristic temperature [6–8]. However, in the proximity of the QCP, since the characteristic temperature is quite low, it is difficult to detect the  $T^2$  dependence. Above the characteristic temperature, it is difficult to determine the temperature dependence of the resistivity because of the subtlety. Actually, as we will show in the following, several types of temperature dependence have been reported for the normal state resistivity in CeNi<sub>2</sub>Ge<sub>2</sub> at ambient pressure.

In order to gain further insight into the normal and superconducting states of CeNi<sub>2</sub>Ge<sub>2</sub> we performed transport measurements in a magnetic field and up to higher pressures. We have determined the upper critical field and the domain of stability under pressure of the superconducting phase. By applying high pressure we move CeNi<sub>2</sub>Ge<sub>2</sub> further from the QCP and we find that a Fermi liquid behaviour of the form  $\rho = \rho_0 + AT^2$  appears. We have also performed susceptibility measurements under pressure and we show that the pressure dependence of the susceptibility and the normal state resistivity can to some extent be understood within a single energy scale.

## 2. Experiment

Single-crystal samples were grown by the Czochralski pulling method using a tetra-arc furnace. In order to improve the quality of crystals, as-grown single crystals were purified by the solid-state electron-transport method with a DC current of  $\sim 1000 \text{ A cm}^{-2}$  under a high vacuum of  $5 \times 10^{-10}$  Torr for 1 week. Several crystals were checked by resistivity measurements. All the resistivity results presented here are on pieces cut from one crystal (No 9), which showed the lowest residual resistivity. Several of these pieces were characterized individually and consistently had residual resistivities of less than 1 and  $3 \mu\Omega \text{ cm}$  for  $\rho \parallel a$  and  $\rho \parallel c$ , respectively. Magnetic susceptibility measurements under high pressure were performed on another single crystal.

The resistivity of crystal 9 at 0 kbar was measured by the four-terminal DC method by using a nano-voltmeter with an He<sup>3</sup> cryostat ( $0.35 \text{ K} < T < 300 \text{ K}$ ). Temperature dependences of the resistivity at very low temperatures were measured by the four-terminal AC method by using a lock-in amplifier (the typical current values go from 0.1 mA to 1 mA) with a conventional dilution refrigerator ( $9 \text{ mK} < T < 0.7 \text{ K}$ ). Four separate experiments under high pressure were performed using different apparatus. Three small pieces with suitable elongated dimensions perpendicular to the  $c$ -axis (9A–9C) were prepared from crystal 9. Sample 9A was measured in a CuBe piston-cylinder type cell up to 17 kbar. In this case resistivity was measured as a function of temperature down to 350 mK at zero magnetic field. Sample 9B was also measured in a piston-cylinder type cell. Sample 9C was measured in a Bridgman type cell with non-magnetic tungsten carbide anvils. This allowed pressures of over 60 kbar to be reached in quasi-hydrostatic conditions. In the latter two cases the sample was measured down to 50 mK and a magnetic field could be applied. In all cases the current was applied in the  $(a, b)$ -plane, and when a field was applied, it was along the  $c$ -axis. The susceptibility at high pressure was measured by using the Faraday method above 2 K under the field of 2 T. The single-crystal sample for magnetic susceptibility measurements was pressurized in a CuBe piston-cylinder type cell up to 8.8 kbar.



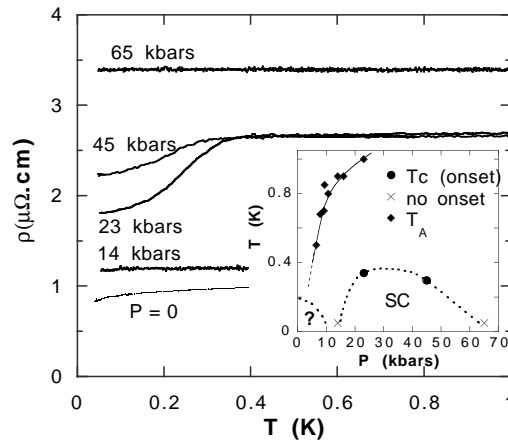
**Figure 1.** The low temperature resistivity of a single crystal of CeNi<sub>2</sub>Ge<sub>2</sub> at ambient pressure. Below 200 mK an anomalous decrease of about 10% is found. This effect can be suppressed by a magnetic field of 0.2 T or by increasing the measuring current density.

### 3. Results and discussion

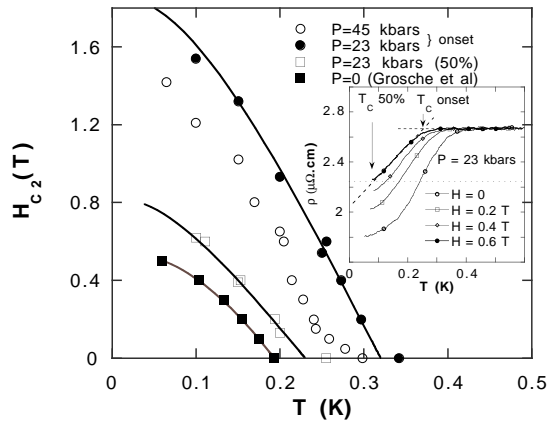
#### 3.1. Superconductivity

The low temperature resistivity at ambient pressure is shown in figure 1. When measured at extremely low current densities, we found a drop in resistance of about 10% below 200 mK. This effect was reproducible on the different samples and is similar to that found by Steglich *et al* [2, 3] and could be tentatively ascribed to the onset of a superconducting transition. As can be seen in the figure this effect is rapidly suppressed by magnetic field (0.2 T) or by a larger measuring current. These results are evidence against bulk superconductivity in this particular sample, even though the residual resistivity is rather low ( $\rho_0 < 1 \mu\Omega \text{ cm}$ ), but clearly the existence or not of superconductivity in CeNi<sub>2</sub>Ge<sub>2</sub> at ambient pressure remains an open question until more reliable results are obtained. Figure 2 shows the effect of pressure on the low temperature resistivity. The resistance drop described above is only just visible on the ambient pressure curve. When a pressure of 14 kbar is applied on sample 9B this effect almost completely disappears. However at 23 kbar (sample 9C) a 30% drop in resistance is found below about 300 mK. This effect is not sensitive to the current density, and, from comparison with the previously published results [5], can probably be attributed to a superconducting transition. As can be seen the effect is still present at 45 kbar, but has disappeared entirely at 65 kbar. We have therefore tentatively sketched the phase diagram of superconductivity under pressure in CeNi<sub>2</sub>Ge<sub>2</sub> in the inset. This diagram is qualitatively in agreement with the one up to about 34 kbar found previously [4].

The detailed analysis of the upper critical field,  $H_{c2}(T)$  can be extremely informative in the heavy fermion superconductors (HFSCs). With the present data this is at present out of reach as the incomplete superconducting transition does not allow us to determine precisely the  $H_{c2}(T)$  diagram. Bearing in mind this limitation it is interesting to qualitatively compare  $H_{c2}$  of CeNi<sub>2</sub>Ge<sub>2</sub> with the theoretical predictions and with the  $H_{c2}(T)$  diagram measured in CeNi<sub>2</sub>Ge<sub>2</sub> at ambient pressure [4], as well as with the other HFSCs. In figure 3 we show the  $H_{c2}(T)$  diagram at 23 and 45 kbar, together with the results at ambient pressure of Grosche *et al* [4]. We performed temperature sweeps at fixed magnetic field (inset) and field sweeps at fixed temperatures. Because of the incomplete nature of the transition, the criterion taken was the



**Figure 2.** The low temperature resistivity of  $\text{CeNi}_2\text{Ge}_2$  at various pressures. The decrease observed at 23 and 45 kbar is taken to indicate the onset of superconductivity. The inset sketches a tentative diagram of the superconducting phases and also shows the temperature  $T_A$  below which a quadratic temperature dependence of the resistivity is found. Lines are guides to the eye.



**Figure 3.** Upper critical field of  $\text{CeNi}_2\text{Ge}_2$ . The full squares represent the data at  $P = 0$  of Grosche *et al* [4]. Points under pressure are obtained either by field sweeps at constant temperature, or temperature sweeps at constant field (inset). The inset also shows the definition of the onset and 50% criteria. Open and full circles represent results at 45 and 23 kbar respectively with the onset criterion. Open squares represent data at 23 kbar with the 50% criterion. The solid lines show calculated weak coupling curves of the upper critical field. The points close to  $T_c$  are discarded because of the anomalous upwards curvature and the  $T_c$  taken for the fit is the extrapolated value. The fitting parameters are  $T_c$ , the gyromagnetic ratio  $g$ ,

$$H'_{c2} = (dH_{c2}/dT)_{T=T_c}$$

and the slope at  $T_c$ :

$$P = 0: T_c = 0.193 \text{ K}; g = 0.75; H'_{c2} = 5.6 \text{ T K}^{-1}$$

$$P = 23 \text{ kbar (onset criterion): } T_c = 0.320 \text{ K}; g = 0; H'_{c2} = 8.3 \text{ T K}^{-1}$$

$$P = 23 \text{ kbar (50% criterion): } T_c = 0.230 \text{ K}; g = 0; H'_{c2} = 5 \text{ T K}^{-1}.$$

onset temperature or field as shown in the inset. With such a broad and incomplete transition, the resulting  $H_{c2}(T)$  diagram is obviously sensitive to the criterion taken so for  $P = 23$  kbar we have also shown the result obtained if we take as a (somewhat arbitrary) criterion the value of

resistivity where 50% of the total resistance loss at zero field has occurred ( $\rho = 2.25 \mu\Omega \text{ cm}$ ). The solid lines show calculated  $H_{c2}(T)$  curves assuming weak coupling in the clean limit which is probably the case for CeNi<sub>2</sub>Ge<sub>2</sub>. The comparison of the superconducting coherence length obtained from the slope of  $H_{c2}(T)$  at  $T_c(H'_{c2})$  with the mean free path estimated from the residual resistivity and the specific heat confirms that this is indeed the case.

From the comparison with the calculated curves, two major phenomena appear, both of which we stress are qualitatively independent of the criterion taken to define  $H_{c2}$ . The values of  $H_{c2}$  at low temperature are extremely high, taking into account the low value of  $T_c$ , and considerably exceed the normal Pauli limit. In fact the data at 23 kbar are close to the theoretical curves obtained with no Pauli limit ( $g = 0$ ). The data at ambient pressure also exceeds the Pauli limit but to a lesser extent ( $g = 0.75$ ). The absence of any Pauli limitation at high pressure might indicate triplet pairing, although strong coupling effects could produce the same result. The second point is that the ratio  $T_c/H'_{c2}$  which is proportional to  $v_F^2$  shows only a weak increase (10–30%) from 0 to 23 kbar whereas from measurements of the decrease of the specific heat coefficient under pressure [9] an increase by a factor of 10–20 would be expected. One possible explanation for the unexpectedly high values of  $H'_{c2}$  at 23 kbar could be a modification of the superconducting order parameter. The usual relation assumes s-wave superconductivity whereas the proportionality between  $v_F^2$  and  $T_c/H'_{c2}$  depends on the order parameter. For example the initial slope for a p-wave state is roughly double that of an s-wave [10]. Of course other phenomena such as the existence of filamentary superconductivity could produce similar results. However if the order parameter of the superconducting phase at high pressure is different from that at ambient pressure, this could explain both the apparent lack of variation of  $v_F$  and the suppression of the Pauli limitation of  $H_{c2}$  with pressure. This would certainly be the most interesting scenario though with the present results it remains somewhat speculative.

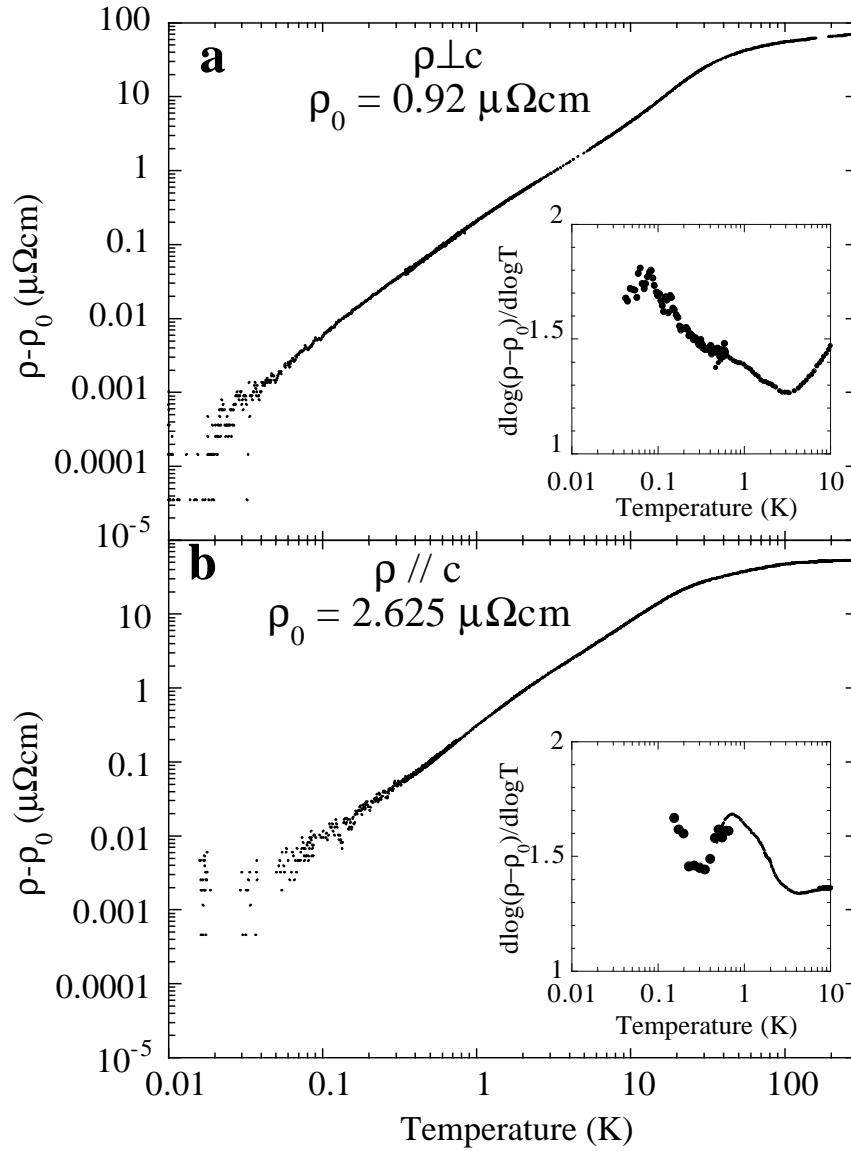
### 3.2. Normal state resistivity and susceptibility

First of all, we focus on the temperature dependence of the normal state resistivity at ambient pressure for the current perpendicular  $\rho^{ab}(T)$  and parallel  $\rho^c(T)$  to the  $c$ -axis. We assume that at low temperature the resistivity of CeNi<sub>2</sub>Ge<sub>2</sub> is approximately described by

$$\rho(T) = \rho_0 + \rho_m(T)$$

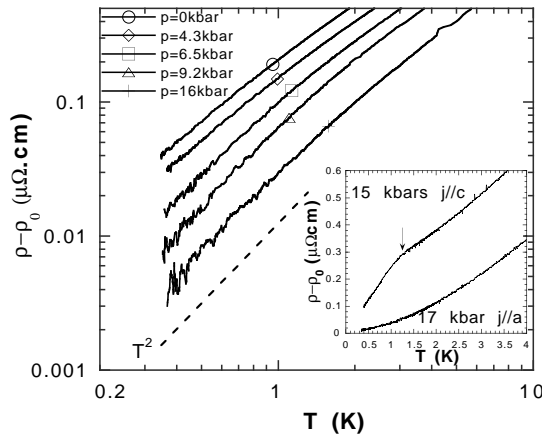
where  $\rho_0$  is the residual resistivity from elastic scatterings due to static imperfections and  $\rho_m(T)$  is the temperature-dependent resistivity from magnetic scatterings, such as spin-fluctuation scattering. For CeNi<sub>2</sub>Ge<sub>2</sub>, even in high quality samples with  $\rho_0 < 1 \mu\Omega \text{ cm}$ ,  $\rho_m(T)$  is much smaller than  $\rho_0$ , therefore the determination of  $\rho_0$  is quite critical. When measurements have been performed down to very low temperature ( $\sim 10 \text{ mK}$ ) we have considered the resistivity at the lowest temperature measured to be  $\rho_0$ . However because of the anomalous resistivity drop observed below 300 mK (see previous section), we have assumed that the saturated value of the residual resistivity at large currents is  $\rho_0$  of the normal-state. Figures 4(a) and 4(b) show  $\rho_m^{ab}(T)$  and  $\rho_m^c(T)$  where the residual resistivities of  $0.920 \pm 0.001 \mu\Omega \text{ cm}$  and  $2.625 \pm 0.003 \mu\Omega \text{ cm}$  for  $\rho^{ab}$  and  $\rho^c$  respectively have been subtracted. At 100 mK the magnetic contributions are  $\rho_m^{ab} = 0.006 \mu\Omega \text{ cm}$  and  $\rho_m^c = 0.009 \mu\Omega \text{ cm}$ . For  $\rho_m^{ab}$ , the magnitude of  $\rho_m$  is comparable with that observed in the typical heavy-fermion compound CeRu<sub>2</sub>Si<sub>2</sub> where  $\rho_m^{ab}$  is  $0.006 \mu\Omega \text{ cm}$  at 100 mK [8].

At  $P = 0$   $\rho(T)$  does not obey a Fermi liquid type law of the form  $AT^2$ . In order to see whether  $\rho_m(T)$  possesses some characteristic exponent  $n$  of the resistivity of the form  $\rho \sim T^n$ , we have calculated the temperature dependence of  $d \log(\rho - \rho_0)/d \log T$  (insets of



**Figure 4.** Log–log plots of  $\rho - \rho_0$  as a function of temperature for  $i \parallel ab$  (top) and  $i \parallel c$  (bottom). Insets show the temperature dependence of the logarithmic derivative  $d \log(\rho - \rho_0)/d \log T$  which represents the exponent  $n$  if the resistivity is of the form  $\rho \sim T^n$ .

figures 4(a) and 4(b)). For  $\rho_m^{ab}$ ,  $d \log(\rho - \rho_0)/d \log T$  gradually approaches the Fermi-liquid value of 2 with decreasing temperature. By extrapolation, we can roughly estimate an upper value for the temperature  $T_A$  below which a  $T^2$  dependence of the resistivity might appear. We find  $T_A \leq 10$  mK. From the extrapolation,  $A$  at 10 mK where  $n(T) \sim 2$ , is estimated to be  $0.7 \pm 0.1 \mu\Omega \text{ cm K}^{-2}$ . For  $\rho_m^c$ ,  $d \log(\rho - \rho_0)/d \log T$  shows an anomalous peak around 0.7 K. This behaviour has been reproduced on different single crystals. The  $T^2$  dependence does not appear at least down to 100 mK. Because of the scatter of the data and the difficulties in



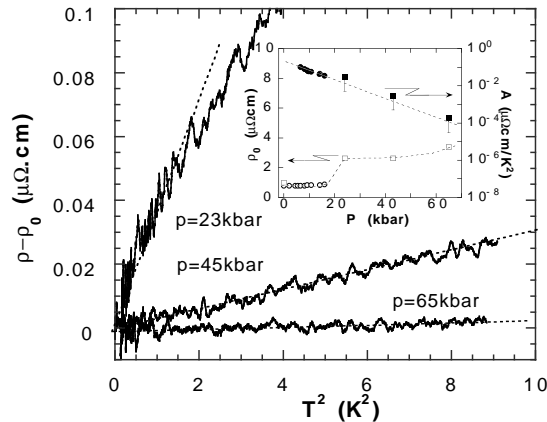
**Figure 5.** Log-log plot of  $\rho - \rho_0$  of sample 9A as a function of temperature for different pressures up to 16 kbar. The inset shows the comparison at approximately 16 kbar between the curves on a different sample ( $\rho_0 = 3 \mu\Omega \text{ cm}$ ) for  $i \parallel c$  and  $i \parallel ab$ . The feature at about 1 K on the  $i \parallel c$  curve is reminiscent of that described by Grosche *et al* [4].

determining  $\rho_0$  we cannot conclude more on the temperature variation of  $d \log(\rho - \rho_0) / d \log T$  of  $\rho_m^c$  below 300 mK. Concerning the resistivity exponent  $n$  of  $\text{CeNi}_2\text{Ge}_2$ , several recent works reported that  $n$  is constant over a wide temperature range, such as  $\rho \sim T^{1.4}$  over a decade below a few kelvin along the  $a$ -axis [11] and  $\rho \sim T^{1.5} - T^{1.37}$  between 0.1 K and 2 K for a high-quality polycrystal sample [3]. This is in disagreement with our result that the resistivity exponent  $n$  of  $\rho_m^{ab}(T)$  and  $\rho_m^c(T)$  is temperature dependent. A recent analysis taking into account the interplay between anisotropic scattering due to spin fluctuations and isotropic impurity scattering predicts a maximum in the temperature dependence of the exponent  $n$  such as we find for  $\rho_m^c(T)$  [12]. It is not clear whether this model could be applied to a pure system with supposedly little disorder like  $\text{CeNi}_2\text{Ge}_2$  but it would be interesting to test systematically the dependence of  $n$  on  $\rho_0$ .

By applying high pressures we expect to drive the system further from the QCP, and a Landau-Fermi-liquid behaviour should appear at much higher temperatures than at 0 kbar. Figure 5 shows the temperature dependence of  $\rho - \rho_0$  for sample 9A for the current along the  $a$ -axis under several pressures. The inset of figure 5 shows a comparison between the curve of  $\rho_m^{ab}(T)$  and  $\rho_m^c(T)$  at similar pressures. The change in slope at around 1 K for  $\rho_m^c(T)$  is reminiscent of the feature found by Grosche *et al* [4] which could indicate another phase transition. Surprisingly no sign of this feature was found in  $\rho_m^{ab}(T)$ . For  $p < 17$  kbar we have determined  $\rho_0$  and  $A$  by fitting the data between 0.35 K and 0.7 K to  $\rho = \rho_0 + AT^n$  where all three parameters  $\rho_0$ ,  $A$  and  $n$  are allowed to vary independently of each other. For  $p = 0$  kbar and 4.3 kbar, the values obtained for  $n$  were not 2, which is consistent with the analysis of the logarithmic derivative. Above 6.2 kbar, from this fit we obtain  $n = 2.0 \pm 0.1$ . The temperature  $T_A$  below which the  $T^2$  dependence is found is shown in the inset of figure 2. With increasing pressure  $T_A$  increases as expected for paramagnetic materials near a magnetic instability, as seen for example in  $\text{CeRu}_2\text{Si}_2$  [13]. At higher pressures the temperature dependent term is too weak to perform the fit. However, as shown in figure 6, the plot of  $\rho$  against  $T^2$  gives a clear straight line at low temperatures, which permits us to estimate  $A$  and  $\rho_0$ .

The pressure dependences of  $\rho_0$  and  $A$  for samples 9A and 9C are shown in the inset of figure 6. For sample 9A,  $\rho_0$  is almost constant between 0 and 17 kbar, which agrees with the previous results reported by Grosche *et al* [5], where an almost constant  $\rho_0$  was reported up to





**Figure 6.**  $\rho - \rho_0$  as a function of  $T^2$  at pressures from 23 to 65 kbar. The inset shows the pressure dependence of  $\rho_0$  for sample 9A (open circles) and 9C (open squares) and the coefficient  $A$  of  $\rho = \rho_0 + AT^2$  for sample 9A (closed circles) and 9C (closed squares).

26 kbar. For sample 9C at 0 kbar,  $\rho_0$  is approximately the same as  $\rho_0$  of sample 9A. However, it shows a steplike increase at higher pressures. We cannot really draw any conclusions from this increase of  $\rho_0$ , because it is possible that it is in part caused by damage to the sample due to the quasi-hydrostatic conditions. Hence, above 23 kbar these  $\rho_0$ -values should be regarded as upper limits. This possible error in  $\rho_0$  could also affect the estimation of  $A$ . If the increase of  $\rho_0$  is an additional constant contribution caused by the appearance of more defects, then it has no consequence on the estimation of  $A$ . On the other hand if cracks appear in the sample which reduce its effective cross section, then the effect on the resistivity is a geometrical factor which would cause us to overestimate the term  $A$ . However we found that the room temperature resistance of the sample decreased with pressure (whereas it *increased* in sample 9A) which implies that the increase of  $\rho_0$  cannot be a pure geometrical factor. We can therefore suppose that the values of  $A$  which we determine are indicative of the intrinsic behaviour. The error bars in the inset of figure 6 show the least favourable situation if the increase of  $\rho_0$  were a purely geometrical factor.

The values of  $A$  obtained for  $\text{CeNi}_2\text{Ge}_2$  are much smaller than those observed in several heavy-fermion superconductors under high pressures. For  $\text{CeCu}_2\text{Si}_2$  [14] and  $\text{CeCu}_2\text{Ge}_2$  [15],  $A$  is reported to be about  $1\text{--}0.5 \mu\Omega \text{ cm K}^{-2}$  around  $P_{max}$ , the pressure where  $T_c$  exhibits a pronounced maximum ( $P_{max} \sim 40$  kbar for  $\text{CeCu}_2\text{Si}_2$  [14] and  $P_{max} \sim 170$  kbar for  $\text{CeCu}_2\text{Ge}_2$  [15]). On the other hand for  $\text{CeNi}_2\text{Ge}_2$  near 30 kbar, where there is a probable maximum of  $T_c$ ,  $A$  is of the order of  $10^{-2} \mu\Omega \text{ cm K}^{-2}$ . This is more than one order weaker than observed in  $\text{CeCu}_2\text{Si}_2$  and  $\text{CeCu}_2\text{Ge}_2$  and is consistent with the specific heat coefficient  $\gamma$  of  $\text{CeNi}_2\text{Ge}_2$  at 0 kbar ( $\sim 320 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ) being about 30% of that for  $\text{CeCu}_2\text{Si}_2$  ( $\sim 1000 \text{ mJ mol}^{-1} \text{ K}^{-2}$ ), because  $A \propto \gamma^2$ . As the density of states at the Fermi level ( $N_F$ ) should be proportional to  $A^{1/2}$ , this suggests that in  $\text{CeNi}_2\text{Ge}_2$   $N_F$  is several times smaller than in  $\text{CeCu}_2\text{Si}_2$  and  $\text{CeCu}_2\text{Ge}_2$  and might explain the lower  $T_c$  at  $P_{max}$  in  $\text{CeNi}_2\text{Ge}_2$  ( $\sim 0.3$  K) compared to  $\text{CeCu}_2\text{Si}_2$  and  $\text{CeCu}_2\text{Ge}_2$  (2–2.5 K). It is pointed out by Miyake *et al* [16] that the coincidence of peaks of  $\rho_0$  and  $T_c$  observed in  $\text{CeCu}_2\text{Ge}_2$  [15] and  $\text{CeCu}_2\text{Si}_2$  [14] under pressure can be understood as due to enhanced valence fluctuations associated with a rapid valence change. In these superconductors, the pressure dependence of  $A$  shows a rapid decrease near  $P_{max}$ , which is thought to be the sign of the valence change. We see no clear indication of this behaviour in

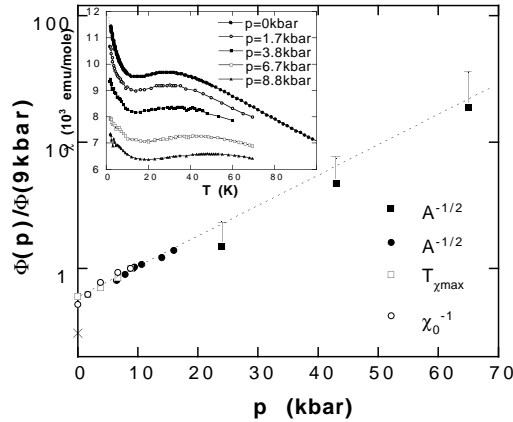
CeNi<sub>2</sub>Ge<sub>2</sub>. However because  $A$  is much weaker, in addition to the facts that the experimental errors are large in this pressure region and our sample is obviously inhomogeneous, we cannot draw clear conclusions as to the pressure dependence of  $A$  (and  $\rho_0$ ) around 30 kbar. Concerning the pressure dependence of  $A$  near the antiferromagnetic instability, it is predicted that  $A$  should diverge as  $A \propto |p - p_c|^{-1/2}$  near the critical boundary based on the self-consistent renormalized spin fluctuation model [6]. We do not observe a linear variation of  $A^{-2}$  with pressure, at least between 9 and 60 kbar, probably because we are too far from the QCP. As of now, we cannot conclude whether an  $A^{-2} \propto |p - p_c|$  behaviour appears near 0 kbar. Precise measurements at very low temperatures and low pressure are needed.

For heavy-fermion systems, the volume dependence of the characteristic energy of the electronic systems  $T^*$ , such as the spin-fluctuation temperature or the Kondo temperature, is usually large. Hence, this is expected to be a dominant factor in the pressure dependence of the coefficient  $A$ . In the Kondo impurity model, thermodynamic and transport properties scale with a single parameter, that is, the Kondo temperature. In a Kondo lattice this simple scaling behaviour should not necessarily hold. However, for several paramagnetic heavy-fermion compounds and valence fluctuation compounds, the volume dependence of thermodynamic and transport properties at low temperatures shows scaling behaviour [17]. This fact suggests that the electronic free energy of these materials is given by a universal function of  $T/T^*(V)$ , where  $V$  is the volume. The relation between volume distortions and electronic states has been described in terms of Grüneisen parameter coupling, that is,

$$\Omega_e = -\frac{\partial \ln T^*}{\partial \ln V} = \kappa^{-1} \frac{\partial \ln T^*}{\partial P} \quad (1)$$

where  $\Omega_e$  is the electronic Grüneisen parameter;  $\kappa = -(1/V)(dV/dP)$  is the isothermal compressibility;  $P$  is pressure.  $\Omega_e$  can be estimated from the pressure dependence of several particular quantities which are proportional to  $T^*$ . If the analogy with the theory of the Kondo impurity effect is valid,  $T^*$  is proportional to the inverse of the magnetic susceptibility at  $T = 0$  ( $\chi_0^{-1}$ ). Through this simple hypothesis,  $T^*$  can be connected to the inverse of the specific-heat coefficient ( $\gamma^{-1}$ ) and also to  $A^{-1/2}$ . In addition, in many paramagnetic systems, the temperature of the maximum in the susceptibility,  $T_{\chi \max}$ , empirically corresponds to  $T^*$ , and the measurement of the pressure dependence of  $T_{\chi \max}$  often permits the determination of  $\Omega_e$  [17, 18]. Thus, to obtain insight into the mechanism of the pressure dependence of  $A$ , it is fruitful to compare these results with the pressure dependence of the susceptibility.

For CeNi<sub>2</sub>Ge<sub>2</sub>, the susceptibility for the field parallel to the c-axis indicates a maximum at  $T_{\chi \max} \sim 29$  K [19], and  $T_{\chi \max}$  shifts to higher temperatures with increasing pressure (inset figure 7). At lower temperatures the susceptibility shows an anomalous up-turn at least down to 2 K. We suppose that this up-turn of the susceptibility is an intrinsic effect and we take the extrapolated value to 0 K as  $\chi_0$ . If we assume that paramagnetic Ce impurities give rise to the up-turn, about 10% of Ce ions must have a magnetic moment of  $2.54 \mu_B$ . This result is unlikely, because such a large amount of paramagnetic impurities should contribute to the residual resistivity, and it would probably be difficult to achieve the low residual resistivity of this sample. According to Aoki *et al* [20], the up-turn can be phenomenologically explained by assuming a particular singularity on the quasiparticle density of states around the Fermi energy, which consistently explains the field dependence of  $\gamma$ . The pressure dependences of  $\ln A^{-1/2}$ ,  $\ln T_{\chi \max}$  and  $\ln \chi_0^{-1}$  are shown in figure 7. These quantities are normalized at 9 kbar. Remarkably the slope of the pressure dependence of  $\ln A^{-1/2}$  above 9 kbar coincides well with those of  $\ln T_{\chi \max}$  and  $\ln \chi_0^{-1}$  below 9 kbar. This implies that the pressure dependence of these quantities is basically dominated by the pressure dependence of  $T^*$ . From the slope below 17 kbar we estimate  $\Omega_e \sim 48$ , by using the isothermal compressibility  $\kappa \sim 0.00115 \text{ kbar}^{-1}$  [21]. This value is about 70% of that observed in CeCu<sub>2</sub>Si<sub>2</sub> ( $\Omega_e = 60\text{--}80$ ) [17, 22]. Above



**Figure 7.** Pressure dependence of  $A^{-1/2}$ ,  $T_{\chi max}$ ,  $\chi_0^{-1}$  with a log scale on the vertical axis. These quantities are normalized at 9 kbar. The dotted line indicates  $\Omega_e \sim 48$ . The x at  $P = 0$  shows the extrapolation of  $A^{-1/2}$  from the logarithmic derivative (see text). The inset shows the magnetic susceptibility of  $\text{CeNi}_2\text{Ge}_2$  under pressure obtained for a magnetic field of 2 T applied along the tetragonal  $c$ -axis. The dotted line shows the extrapolation of  $\chi_0$ .

23 kbar,  $\ln A^{-1/2}$  for sample 9C is consistent with this relation within the experimental uncertainties mentioned above.

It should be noted here that a magnetic field generally pushes electronic systems away from the QCP, and destroys the anomalous behaviours. Therefore, it is surprising that the scaling behaviour holds between  $\chi_0^{-1}$  and  $T_{\chi max}$  measured at 2 T and  $A^{-1/2}$  measured at 0 T. Actually, it has been confirmed that the effect of the field is rather strong at 0 kbar. In the field range from 1 to 7 T (unpublished data),  $\chi_0$  increases steeply with decreasing field. Therefore,  $\chi_0^{-1}$  in the limit of  $H = 0$  is smaller than shown in figure 7. In addition, the extrapolated value for  $A^{-1/2}$  at 0 kbar found from the logarithmic derivative is also much lower than the dotted line (shown as  $\infty$  in figure 7). If  $\ln \chi_0^{-1}$  and  $\ln A^{-1/2}$  at 0 kbar are smaller than the value of the dotted line, the initial slopes of the pressure dependence of  $\ln \chi_0^{-1}$  and  $\ln A^{-1/2}$  should be much larger which means that  $\Omega_e$  calculated from  $\chi_0^{-1}$  and  $A^{-1/2}$  is much larger than 48 in the limit of  $H = 0$  and  $P = 0$ . On the other hand, it is remarkable that  $T_{\chi max}$  is not affected by the field between 1 and 7 T. This fact implies that the simple scaling behaviour may exist at high pressure but is not obeyed in  $\text{CeNi}_2\text{Ge}_2$  near 0 kbar and low magnetic field.

#### 4. Conclusion

We have established a preliminary phase diagram for superconductivity in  $\text{CeNi}_2\text{Ge}_2$ . We find that  $T_c$  goes through a maximum, probably around 30 kbar, and that superconductivity seems to disappear above 65 kbar. The upper critical field is found to exceed 1.5 T which is extremely high considering the low value of  $T_c$ . The normalized values of  $H_{c2}$  and  $dH_{c2}/dT$  at  $T_c$  are larger than those for most of the other known heavy-fermion superconductors, and the value of  $H_{c2}$  at low temperature greatly exceeds that expected for normal Pauli limiting, probably indicating triplet superconductivity or strong coupling effects. The high value of the slope  $dH_{c2}/dT$  at  $T_c$  might also be an indication of a change in the order parameter between the superconducting phases at ambient pressure and high pressure, as the deduced Fermi velocities are not compatible with the decrease of the specific heat coefficient. The normal state resistivity at 0 kbar does not show the quadratic temperature dependence at least down to

50 mK. This is attributable to the low characteristic temperature of the Fermi-liquid behaviour in CeNi<sub>2</sub>Ge<sub>2</sub> due to the proximity of the magnetic instability. For the resistivity perpendicular to the *c*-axis, the exponent *n* of the resistivity of the form  $\rho \sim T^n$  increases towards 2 at very low temperatures, and possibly reaches 2 below 10 mK. From the normal state resistivity and susceptibility measurements under high pressures, we conclude that the  $\rho_0 + AT^2$  dependence of the resistivity observed in CeNi<sub>2</sub>Ge<sub>2</sub> under high pressure for the current perpendicular to the *c*-axis is intrinsic behaviour, and the strong pressure dependence of *A* is explained by the volume dependence of a characteristic energy  $T^*$  in terms of the Grüneisen parameter coupling although this simple scaling probably is not obeyed close to the critical point in the limit  $P = 0$  and  $B = 0$ . The pressure dependence of *A* in CeNi<sub>2</sub>Ge<sub>2</sub> seems comparatively simple in relation to CeCu<sub>2</sub>Ge<sub>2</sub> and CeCu<sub>2</sub>Si<sub>2</sub> which have similar superconducting phase diagrams.

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