

## Non-Doniach-type phase diagram of CeNiGe<sub>2</sub>

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(Received 20 December 2011; published 9 January 2012)

The heavy-fermion antiferromagnet CeNiGe<sub>2</sub> was investigated under pressure by resistivity and ac calorimetry up to 4 GPa and down to 40 mK. The two magnetic transitions found in both resistivity and specific heat at 0.1 GPa at  $T_{N1} = 3.95$  and  $T_{N2} = 3.21$  K are replaced by a single one at 0.7 GPa and 2.81 K. Increasing pressure initially reduces this further, however, at about 1.7 GPa, a new transition appears, accompanied by a marked change in the pressure dependence of the ordering temperatures, the temperature dependence of the resistivity, and the residual resistivity; the latter indicates a marked change in the quantum fluctuations present. There are signs that this new transition has some first-order character. The phase diagram of CeNiGe<sub>2</sub> bears little resemblance to the Doniach phase diagram widely used to classify heavy-fermion compounds.

DOI: [10.1103/PhysRevB.85.033101](https://doi.org/10.1103/PhysRevB.85.033101)

PACS number(s): 71.27.+a, 75.30.Kz, 75.30.Mb, 75.40.Cx

Cerium-based heavy-fermion intermetallic compounds have been studied extensively for many years due to their diverse and fascinating range of ground states. The ternary Ce-Ni-Ge family displays the entire range of behavior seen in these systems: ferromagnetic, antiferromagnetic (AFM), heavy fermion (HF), superconducting, non-Fermi liquid, and intermediate valent (IV) types of behavior are all found either under ambient conditions or with the application of hydrostatic pressure.<sup>1</sup> The ground state is largely determined by the configuration of the Ce 4*f* electron: its degree of localization on the Ce ion, and the extent to which its magnetic moment is screened by conduction electrons (the Kondo effect).

There is a consensus that the magnetic phase diagram of most Ce compounds can be fitted into a single scheme, known as the Doniach diagram, governed by the magnitude of the exchange interaction between the Ce 4*f* and conduction electrons.<sup>2</sup> This is strongly affected by changes in unit cell volume, which can be controlled by pressure or chemical substitution. Compression tends to move the ground state toward a nonmagnetic limit in the sequence AFM → HF → IV. The theoretical model considers competing RKKY and Kondo interactions, which respectively promote and suppress magnetic order; this predicts an AFM ordering temperature  $T_N$  that first increases with pressure, and then is suppressed to zero in a second-order manner as the local moments are screened completely. The point at which  $T_N$  reaches zero is known as the quantum critical point (QCP), around which many novel phenomena have been found, such as unconventional superconductivity and non-Fermi liquid behavior. The heavy-fermion antiferromagnet CeNiGe<sub>2</sub>, however, is an exception to this scheme.

We present resistivity and specific heat measurements under high pressure on CeNiGe<sub>2</sub>, which lies on the boundary between AFM, HF, and IV behavior. It is a highly anisotropic compound, crystallizing in the orthorhombic CeNiSi<sub>2</sub>-type structure (space group *Cmcm*). The easy magnetic direction was found to be parallel to the crystallographic *a* axis (resolving some earlier ambiguity).<sup>3</sup> The Sommerfeld coefficient  $\gamma$  has been estimated to be 100 mJ/mole K<sup>2</sup> at  $p = 0$ , though its determination is complicated by the presence of magnetic order;<sup>4,5</sup> at ambient pressure CeNiGe<sub>2</sub> shows two

antiferromagnetic ordering temperatures, at  $T_{N1} = 3.2$  K and  $T_{N2} = 3.9$  K. The magnetic structure is currently unknown, though it is of a complex incommensurate nature, as is that of the isostructural compound CeRhGe<sub>2</sub>.<sup>6,7</sup>

The isostructural sister compound CeNiSi<sub>2</sub> is an intermediate valence system with a unit cell volume about 4% smaller than CeNiGe<sub>2</sub>. Several investigations have been carried out on the intermediate alloys CeNi(Ge<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub>.<sup>5,8-11</sup> These show a disappearance of magnetism for  $x \simeq 1$ , and some signs of a QCP. They also show a nonlinear decrease of  $T_N$  with  $x$ , and a transition to IV behavior as  $x \rightarrow 1$ . By applying pressure to CeNiGe<sub>2</sub>, we wished to see cleanly the effect of reducing the cell volume and suppressing magnetic order, if possible to pass through a QCP and eventually reaching the IV state at high enough pressure. However, several intriguing phenomena appeared even before these features were reached, and these are subject of this paper.

The sample was selected from single crystals of CeNiGe<sub>2</sub> grown by the In-flux method as described previously.<sup>3</sup> It was cut and polished to  $90 \times 200 \times 20 \mu\text{m}^3$ . Six 10- $\mu\text{m}$  wires were spot-welded to the sample so that the electrical current for resistivity measurements was oriented along the *a* axis. They consisted of two AuFe(0.07 at %)/Au thermocouples at either end of the sample, and a pair of voltage contacts suitable for four-point resistance measurements. Knowledge of the sample geometry enabled us to estimate the absolute resistivity to within ~16%.

It is generally very difficult to measure specific heat under pressure due to the tiny size of the samples and overwhelming addenda contribution. However, the ac calorimetry method enables the sample specific heat,  $C_p$ , to be determined in a semiquantitative way, despite these drawbacks.<sup>12</sup> An alternating heating current of up to 4.7 mA was applied to one thermocouple, and the resulting temperature oscillations measured at the other via lock-in detection. The system can be modeled as a heat capacity  $C$  connected via a thermal resistance  $K$  to a bath at temperature  $T_0$ , giving a characteristic sample relaxation frequency  $\omega_{c1} = K/C$ . The equilibration time between the thermocouple, heater, and sample is combined into a second (higher) characteristic frequency  $\omega_{c2}$ . At various temperatures, the frequency dependence of the

thermocouple signal  $\tilde{V}_{ac}$  was measured, and the amplitude fitted to the formula:

$$|\tilde{V}_{ac}| = \frac{A}{\omega} [1 + (\omega/\omega_{c1})^{-2} + (\omega/\omega_{c2})^2]^{-1/2}, \quad (1)$$

where  $A$  is a constant, proportional to the heating power and thermocouple thermopower. Provided that the working frequency  $\omega \ll \omega_{c2}$ , the model can be simplified, neglecting  $\omega_{c2}$ . We extracted the heat capacity  $C$  from the amplitude and phase of the temperature oscillations as described in Ref. 13. The parameters  $\omega_{c1}$  and  $\omega_{c2}$  decreased by a factor of ten from 4.2 to 1.5 K, and as  $\omega_{c2} \sim 2\omega_{c1}$ , we chose a working frequency slightly below  $\omega_{c1}$  at 1 K, typically  $\sim 100$  Hz. Usually the temperature dependence was measured at two or more frequencies, and the calculated specific heat compared. A large disagreement indicated a decoupling of the sample and thermocouple, and with a measurement at  $\omega \ll \omega_{c1}$  the temperature offset of sample above the background temperature could be estimated, and was typically in the range 0.2–10 mK.

This method has very high sensitivity, but it is difficult to ascertain the absolute value of  $C_p$ , owing to uncertainties in the thermocouple calibration under pressure, the contribution of the pressure medium, diamonds and wires, and the absolute power delivered to the sample. However, all of these are likely to vary slowly with pressure, so we can make definite observations of phase transitions, including the shape and size of any jump in specific heat.

High pressure was generated using the clamped diamond anvil cell (DAC) method, with NaCl as a pressure medium. Force was applied at room temperature, and the ruby fluorescence method used to determine the pressure,  $p$ , at around 25 and 300 K; we estimated the pressure gradients to be about 10%. A considerable loss of pressure occurred on cooling from room temperature to around 40 K, however, on further cooling, little hysteresis was seen in the resistivity, so we believe the pressure remained constant below this temperature. Resistance measurements were carried out in a dilution cryostat, and ac calorimetry in a  $^4\text{He}$  dewar up to 1.4 GPa, and in a dilution cryostat above this pressure. For the latter, the heating current was reduced as the temperature decreased, and the signal scaled appropriately.

Figures 1 and 2 show the resistivity and ac specific heat of CeNiGe<sub>2</sub> as a function of temperature and pressure, below 5 K. The compound displays rather different behavior above and below about 1.7 GPa, so the resistivity results have been divided for clarity, Fig. 1(a) showing those up to 1.9 GPa (region I) and Fig. 1(b) those at high pressure (region II). The curves at 1.9 GPa are repeated for comparison.

The resistivity of CeNiGe<sub>2</sub> initially decreases on cooling from room temperature, most likely due to a reduction of phonon scattering. This is followed by two broad maxima in  $\rho(T)$  at  $T_2^{\max}$  ( $\sim 60$  K) and  $T_1^{\max}$  ( $\sim 5$  K at ambient pressure). This behavior, reported also in Ref. 3, is typical of a Kondo lattice system subject to crystal field splitting of the  $f$  level. Below  $T_1^{\max}$ , magnetic ordering can be discerned, sometimes by a clear kink in the resistivity, or at least by an anomaly observable in  $d\rho/dT$ .

The two antiferromagnetic transitions at close to ambient pressure are easily identified as separate peaks in the ac

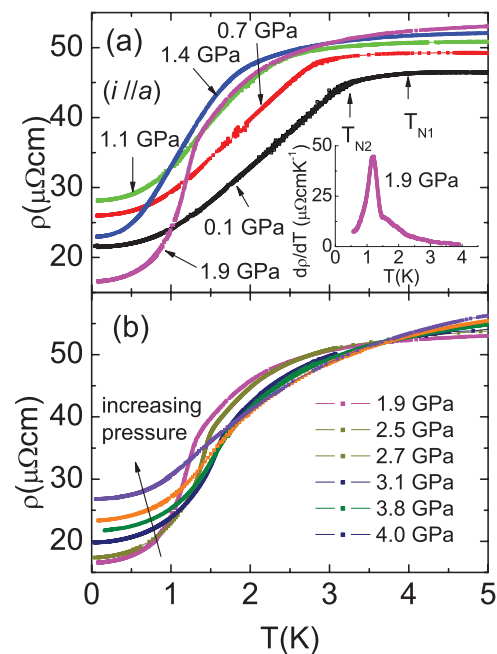


FIG. 1. (Color online) Temperature dependence of resistivity up to (a) and above (b) 1.9 GPa, with the curve at 1.9 GPa repeated for comparison. The position of the vertical arrows showing  $T_{N1}$  and  $T_{N2}$  were determined from the inflection points of the specific heat. Note the early disappearance of the second transition, and the dramatic change of behavior in the resistivity between 1.4 and 1.9 GPa. The inset shows  $d\rho/dT$  at 1.9 GPa; a shoulder is visible, indicating the higher-temperature transition.

specific heat (see Fig. 2) at temperatures  $T_{N1} = 3.95$  and  $T_{N2} = 3.21$  K, in agreement with previous reports.<sup>3</sup> The low-temperature kinks in resistivity corresponded exactly to peaks in the specific heat at all pressures up to 4 GPa. At 0.1 GPa, the anomaly in resistivity at  $T_{N1}$  is very weak, and can only be seen clearly by taking the derivative  $d\rho/dT$ . There is also a broad Kondo maximum  $T_1^{\max}$  at 4.5 K.

Pressure affects the transition temperatures as follows [see Fig. 3(a)]. As the pressure starts to increase, the two transitions are replaced by only one; at 0.7 GPa, a single peak can be identified in  $C_p$  at a temperature  $T_M = 2.81$  K. On further

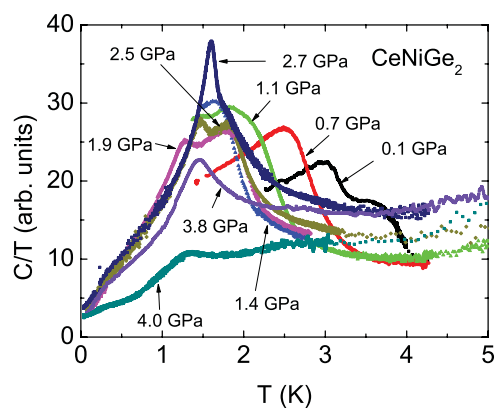


FIG. 2. (Color online) The ac specific heat as a function of temperature. Note that the results at 3.1 GPa are omitted due to experimental difficulties.

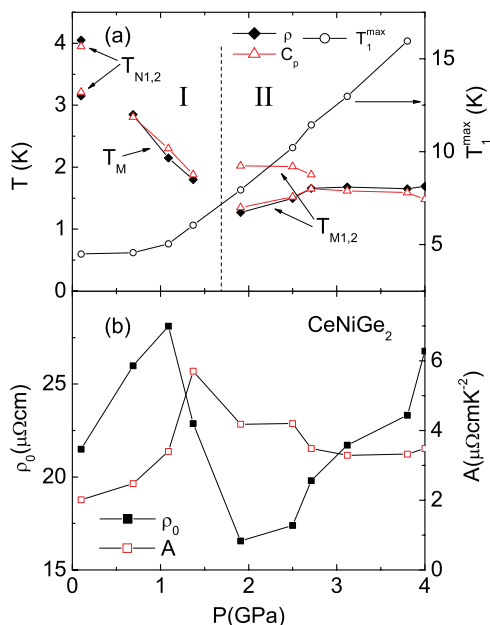


FIG. 3. (Color online) (a) Left hand scale: ordering temperature determined by resistivity (inflection in  $d\rho/dT$ ) (filled diamonds) and specific heat (open triangles, also determined by inflection point on the high  $T$  side of peak). Labels as described in text. Right hand scale: Kondo coherence temperature  $T_1^{\max}$ . (b) Coefficients of a fit to  $\rho(T) = \rho_0 + AT^2$  below 0.5 K.

increasing the pressure, initially  $T_M$  decreases linearly with  $p$ . At 1.9 GPa, a new transition appears at  $T_{M2} = 1.35$  K, this is clearly visible in both resistivity and specific heat. A second transition is found at  $T_{M1} = 2.02$  K, barely visible in resistivity but with a clear signature in  $C_p$ . From this pressure onwards, the temperatures  $T_{M2}$  and  $T_{M1}$  no longer decrease monotonically.  $T_{M2}$  rises slightly to a broad maximum of around 1.65 K before saturating at  $\sim 1.5$  K, while  $T_{M1}$  appears to fall slightly and then converge with  $T_{M2}$ , though the signature of this transition becomes weaker and is no longer visible above 2.7 GPa.

The low-temperature maximum in resistivity  $T_1^{\max}$  is proportional to the Kondo temperature  $T_K$ .  $T_1^{\max}$  initially increases quite slowly with pressure, then much more quickly above  $\approx 1$  GPa.

The temperature dependence of the resistivity as  $T \rightarrow 0$  gives an indication of the nature of elementary electronic excitations. Below 0.5 K,  $\rho(T)$  can be fitted to a power law,  $\rho = \rho_0 + AT^n$ , with  $n$  slightly greater than two. This is typical of Fermi-liquid behavior in the presence of some spin-wave excitations.  $\rho_0$  reflects scattering from static disorder, and  $A$  is determined by dynamic scattering of the quasiparticles, where the bare electron-electron interactions are strongly renormalized by low-energy excitations in these systems. As the pressure is increased up to 1.4 GPa,  $A$  rises by nearly a factor of three [see Fig. 3(b),  $n$  set to two], indicating an increase of the Sommerfeld coefficient from 448 to 755  $\text{mJ mole}^{-1}\text{K}^{-2}$ , derived by the Kadowaki-Woods relation for correlated systems.<sup>14</sup> After the appearance of  $T_{M2}$ ,  $A$  decreases markedly, and remains roughly constant up to 4 GPa. N.B. the low-temperature resistivity maximum  $T_1^{\max}$  remains well separated from  $T_2^{\max}$ , implying that  $T_K$  remains below

the crystal field splitting  $\Delta$ , and a ground-state degeneracy of  $N = 2$  can be assumed.

The residual resistivity  $\rho_0$  is usually thought to reflect the impurity concentration in a sample, which is not affected by pressure. The large variations of  $\rho_0$  with pressure in  $\text{CeNiGe}_2$  are therefore surprising.  $\rho_0$  initially starts to increase, however, by 1.4 GPa it has fallen sharply, continuing to drop further up to 1.9 GPa. Above this pressure, the residual resistivity increases monotonically. This variation of  $\rho_0$  is contrasted by the smooth pressure evolution of the resistivity at higher temperature. It is especially striking to compare the resistivity curves at 1.1 and 1.9 GPa. Above  $T_{M2}$ , the curves are nearly identical, but the resistivity drops sharply below the transition to a lower value of  $\rho_0$ . Interestingly, the resistivity curve at 1.4 GPa is an intermediate case, with no visible transition, perhaps indicating precursor effects.

An enhancement of the residual resistivity, and particularly a peak of the  $A$  coefficient of the resistivity, is often found at an antiferromagnetic QCP, where abundant low-energy excitations can strongly renormalize the electronic effective mass and alter impurity potentials. The low-pressure (region I) behavior of  $\text{CeNiGe}_2$  strongly resembles the approach to such a QCP, however, anomalies associated with magnetic order persist up to the highest pressures so far measured. Extrapolating the decrease of  $T_M$  leads to a projected QCP at around 3 GPa. The system effectively avoids this QCP, with a new transition  $T_{M2}$  appearing.

The pressure evolution of  $T_{M2}$  is also rather unexpected. The transition temperature appears to saturate with increasing pressure, and the specific heat signature first sharpens before growing weaker (see Fig. 2). The sharpening of the peak implies that pressure gradients are not a serious problem, though to be sure, measurements in a hydrostatic medium are necessary. The collapse of the specific heat jump at higher pressure could be explained by phase separation, if the transition at  $T_{M2}$  has some first-order character.

The drop in residual resistivity above 1.4 GPa is not compatible with the opening of a new gap on the Fermi surface, which would increase  $\rho_0$ . However,  $\text{CeNiGe}_2$  is a highly anisotropic compound, and a potential model involves the existence of multiple coupling parameters: (i) a strong in-plane  $f$ - $d$  hybridization  $J_{f-d}$  and (ii) an interlayer coupling  $J_{\perp}$  generating long-range magnetic order. This was proposed to explain the change from ferro- to antiferromagnetism in  $\text{CePd}_2\text{Al}_2\text{Ga}$  under pressure,<sup>15</sup> where different pressure dependencies of  $J_{f-d}$  and  $J_{\perp}$  lead to competition between multiple ground states. In  $\text{CeNiGe}_2$ , as the balance between these coupling strengths is altered by pressure, a new ground state appears above 1.4 GPa. At temperatures above the ordering transition, the principle scattering is from spin disorder, which varies smoothly with pressure. The different magnetic structures will be associated with different fluctuations: thermal and quantum in the vicinity of a quantum phase transition. While the thermal fluctuations are quenched as  $T \rightarrow 0$ , quantum fluctuations remain, and fluctuation-enhanced impurity scattering is strongly modified by the change in elementary excitations.

The smooth variation of the resistivity with pressure at high temperature, up to 300 K, with no change in the overall shape, implies that there were no problems with the electrical contacts, which could otherwise cause shifts

in the resistance measured and hence the inferred absolute resistivity. It also rules out structural changes; this is supported by preliminary x-ray measurements, and also by analogy with the CeNi(Ge<sub>1-x</sub>Si<sub>x</sub>)<sub>2</sub> series, in which the end members have the same structure. A similar saturation of  $T_N$  was also found in CeNiGe<sub>2</sub> by Ohashi *et al.*<sup>16,17</sup> in a large-volume cell with a liquid medium, so it is unlikely that poor pressure conditions are responsible for the observed behavior.

In conclusion, the evolution of magnetic order in CeNiGe<sub>2</sub> appears to contradict the Doniach model, being very different from that seen in compounds considered archetypical of the Ce-based HF family such as CeIn<sub>3</sub>. It has been observed experimentally that bare QCPs are rarely if ever found in real systems, and tend to be obscured by some other exotic phase. It may be that CeNiGe<sub>2</sub> is a further example of this phenomenon.

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