

Evidence for Unconventional Superconducting Fluctuations in Heavy-Fermion Compound CeNi₂Ge₂

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We present evidence for unconventional superconducting fluctuations in a heavy-fermion compound CeNi₂Ge₂. The temperature dependence of the ⁷³Ge nuclear-spin-lattice-relaxation rate $1/T_1$ indicates the development of magnetic correlations and the formation of a Fermi-liquid state at temperatures lower than $T_{FL} = 0.4$ K, where $1/T_1T$ is constant. The resistance and $1/T_1T$ measured on an as-grown sample decrease below $T_c^{\text{onset}} = 0.2$ K and $T_c^{\text{NQR}} = 0.1$ K, respectively; these are indicative of the onset of superconductivity. However, after annealing the sample to improve its quality, these superconducting signatures disappear. These results are consistent with the emergence of unconventional superconducting fluctuations in close proximity to a quantum critical point from the superconducting to the normal phase in CeNi₂Ge₂.

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Unconventional superconductivity observed in the vicinity of the antiferromagnetic (AFM) quantum critical point (QCP) has been one of the most important issues in cerium (Ce)-based heavy-fermion (HF) compounds, since it was universally found at the border of antiferromagnetism in CeCu₂Si₂, CeRh₂Si₂, CeIn₃, CePd₂Si₂, and CeRhIn₅.¹⁾ Therefore, it is believed that superconductivity in these compounds is mediated by the magnetic fluctuations induced near the AFM QCP.²⁾ Recently, Yuan *et al.* showed that a robust superconducting (SC) phase under pressure in the prototype HF superconductor CeCu₂Si₂ is divided into two SC domes in CeCu₂(Si_{1-x}Ge_x)₂. Since the second SC phase emerges far from the AFM QCP in CeCu₂(Si_{1-x}Ge_x)₂, a valence-fluctuation-mediated SC mechanism is proposed for the onset of this SC phase.^{3,4)} However, thus far, there are few experimental examples for these types of HF superconductivity. Therefore, the mechanism of superconductivity in HF compounds is still under debate from various viewpoints.

The HF compound CeNi₂Ge₂ crystallizes in the ThCr₂Si₂ structure. The measurements of resistivity and specific heat at low temperatures clearly revealed non-Fermi-liquid-like behaviors associated with antiferromagnetism; $\Delta\rho \propto T^n$ ($n = 1.2-1.5$) and $\Delta C/T \propto \ln T$.⁵⁻⁷⁾ In fact, a small amount of substitution for the Ni site in Ce(Cu_{1-x}Ni_x)₂Ge₂ and Ce(Ni_{1-x}Pd_x)₂Ge₂ leads to an AFM order by expanding its lattice volume.⁸⁻¹⁰⁾ Thus, CeNi₂Ge₂ is located near the AFM QCP. Remarkably, there exist several reports indicating that resistance becomes zero below $T_c \sim 0.2$ K in CeNi₂Ge₂, suggesting the onset of superconductivity.^{6,11)} Therefore, it is suggested that magnetic fluctuations with regard to the AFM QCP are responsible for the onset of superconductivity in this compound. However, since superconductivity in this

compound strongly depends on the sample preparation method and/or the nominal stoichiometry in the Ni element,¹¹⁾ experiments revealing bulk superconductivity have not been reported to date. It should be noted that two SC domes have also been reported in CeNi₂Ge₂ from resistivity measurements under pressure.^{12,13)}

In this letter, we report systematic studies of resistivity and ⁷³Ge nuclear quadrupole resonance (NQR) in an as-grown and an annealed sample of CeNi₂Ge₂. The NQR spectrum does not reveal any trace of a magnetic order down to 0.03 K. The temperature (T) dependence of the nuclear spin-lattice relaxation rate $1/T_1$ indicates the growth of magnetic correlations followed by an emergence of the Fermi-liquid state below $T_{FL} = 0.4$ K, where $1/T_1T$ is constant. A decrease in both resistance and $1/T_1T$ are observed below $T_c^{\text{onset}} = 0.2$ K and $T_c^{\text{NQR}} = 0.1$ K in the as-grown sample, respectively. These anomalies are related to the onset of superconductivity because the application of a tiny magnetic field causes $1/T_1T$ to remain constant. On annealing to improve the quality, the anomalies with regard to the onset of superconductivity disappear. Importantly, the signature towards SC transition has been microscopically investigated by the NQR- T_1 measurement, which reveals a reduction without a coherence peak in $1/T_1$ just below T_c . However, the result that zero resistance is *not* observed could be attributed to the SC fluctuations due to the proximity with a SC QCP.

High-quality single crystals of CeNi_{2.02}Ge₂ were grown by the Czochralski method and moderately crushed into grains in order to enable easy penetration of the rf pulses into the samples. However, to avoid crystal distortions, the size of the grains is kept larger than 100 μm . Note that the onset of superconductivity in this compound is extremely sensitive to the sample preparation method and/or the nominal stoichiometry in the Ni element. The sharpest SC transition

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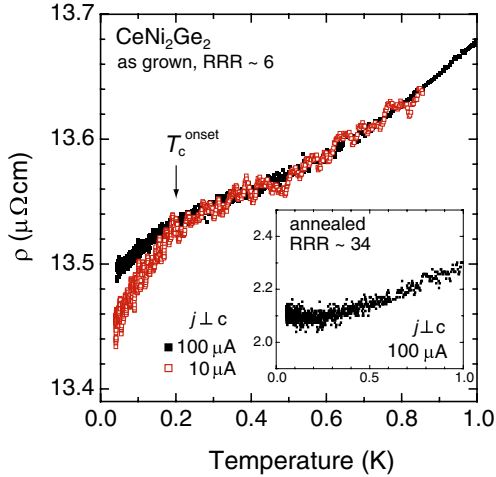


Fig. 1. (Color online) Temperature and current dependences of resistivity for the as-grown sample of CeNi_2Ge_2 . Solid arrow indicates T_c^{onset} . The inset shows the temperature dependence of resistivity for the annealed sample (see text).

was reported for the Ni-rich sample $\text{CeNi}_{2.02}\text{Ge}_2$.¹¹⁾ The measurements of resistance and ^{73}Ge NQR with nuclear spin $I = 9/2$ were performed using an almost 100% ^{73}Ge enriched sample. A single crystal is used for the resistivity measurement. The T dependence of resistivity was measured in a zero field ($H = 0$) by the conventional four-probe method. The current flows perpendicular to the c axis. The T dependences of ^{73}Ge NQR spectra and $1/T_1$ were measured at $H = 0$ down to $T = 0.03$ K using a $^3\text{He}/^4\text{He}$ dilution refrigerator. In order to detect the possible onset of some magnetic ordering at low temperatures, the NQR spectrum for the $1\nu_Q$ ($\pm 1/2 \leftrightarrow \pm 3/2$) transition was precisely measured by the Fourier transform method for spin-echo signals.

Figure 1 and the inset show the T dependences of resistance for the as-grown and annealed single crystals, respectively. Note that the resistance at the ab -plane decreases for the as-grown sample below $T_c^{\text{onset}} = 0.2$ K, but it does not drop to zero; it is consistent with the previous results.¹³⁾ In addition, this reduction depends on the magnitude of current, which indicates the onset of superconductivity. As shown in the inset of Fig. 1, on annealing to improve the quality, the residual resistivity ratio (RRR) increases from $\text{RRR} = 6$ to 34 for the annealed sample. Nevertheless, the SC anomaly disappears. This is an underlying issue to be addressed on the basis of the microscopic measurements of the ^{73}Ge NQR spectrum and $1/T_1$ in order to clarify microscopically the non-Fermi-liquid-like behaviors reported thus far and a possible signature of the onset of superconductivity.

Figure 2(a) shows the ^{73}Ge NQR spectra at $T = 1.5$ K, which consist of four equally spaced NQR spectra with $\nu_Q = 1.632$ MHz and the asymmetry parameter $\eta = 0$ due to the uniaxial symmetry. Here, ν_Q is defined as a parameter in the following Hamiltonian:

$$\mathcal{H}_Q = \frac{h\nu_Q}{6} \left(3I_z^2 - I^2 + \frac{1}{2} \eta (I_+^2 + I_-^2) \right), \quad (1)$$

where

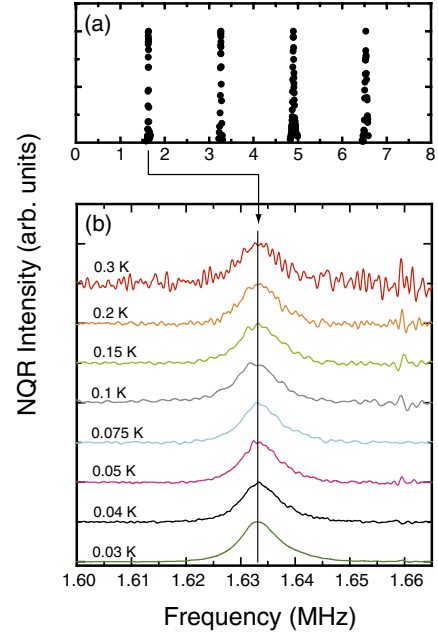


Fig. 2. (Color online) (a) ^{73}Ge NQR spectra at $T = 1.5$ K (see text). (b) Temperature dependence of the ^{73}Ge $1\nu_Q$ -NQR spectrum in CeNi_2Ge_2 . Solid line denotes the peak position.

$$\nu_Q = \frac{eQV_{zz}}{6I(2I+1)} \quad (2)$$

and

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}. \quad (3)$$

Note that the full width at half maximum (FWHM) for the $1\nu_Q$ -NQR spectrum is quite sharp at $\text{FWHM} = 8$ kHz, confirming the high quality of the sample used in this study. The NQR spectra can indicate the emergence of a static magnetic order for CeNi_2Ge_2 from the splitting and/or the broadening of the $1\nu_Q$ -NQR spectrum due to the appearance of an internal field, if any. Since the FWHM of the $1\nu_Q$ -NQR spectrum does not exhibit any change as shown in Fig. 2(b), there is no evidence for a magnetic order and/or a structural change down to 0.03 K in the as-grown and annealed samples of CeNi_2Ge_2 .

Next, we present the T dependence of $1/T_1$ that reveals low-energy excitations relevant to non-Fermi-liquid-like behaviors and the possible onset of superconductivity in CeNi_2Ge_2 . Figures 3(a) and 3(b) show the typical data sets of the time dependence of nuclear magnetization of the $1\nu_Q$ transition at $T = 0.3$ and 0.04 K, respectively. They can be fitted by theoretical curves (solid lines) with a single T_1 component according to eq. (4)¹⁴⁾ as indicated in Fig. 3. Note that the saturation pulse width is reduced below $T = 0.1$ K to avoid some heating effect caused by the application of a radio frequency field at low temperatures.

$$1 - \frac{M(t)}{M_0} = \frac{1}{132} \exp\left(\frac{-3t}{T_1}\right) + \frac{45}{572} \exp\left(\frac{-10t}{T_1}\right) + \frac{49}{165} \exp\left(\frac{-21t}{T_1}\right) + \frac{441}{715} \exp\left(\frac{-36t}{T_1}\right) \quad (4)$$

Figure 4 shows the T dependence of $1/T_1T$ under zero field ($H = 0$) (circle), $H = 0.03$ T (triangle), and $H = 0.1$ T

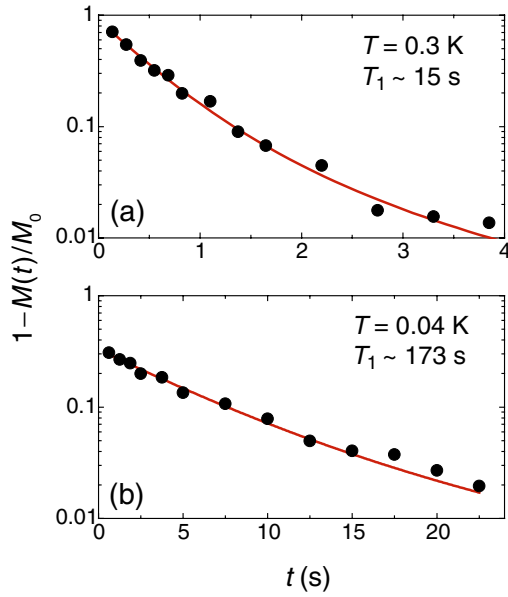


Fig. 3. (Color online) Recovery curves of the nuclear magnetization of ^{73}Ge at (a) $T = 0.3\text{ K}$ and (b) $T = 0.04\text{ K}$ in CeNi_2Ge_2 . The red curves are fitted according to eq. (4).

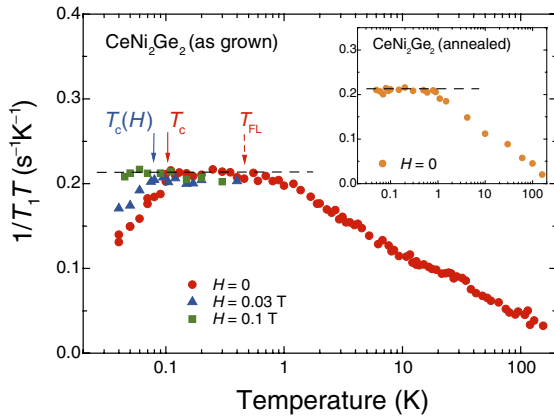


Fig. 4. (Color online) Temperature dependence of $1/T_1T$ for CeNi_2Ge_2 (solid circle). Solid triangles and squares indicate the temperature dependence of $1/T_1T$ under a magnetic field of $H = 0.03$ and 0.1 T , respectively. Dotted line indicates a $1/T_1T = \text{const}$ law. Solid and dashed arrows indicate T_c and $T_c(H)$, and T_{FL} (see the text), respectively.

(square) in the T range of $0.04\text{--}150\text{ K}$. The $1/T_1T$ at $H = 0$ increases as the temperature decreases to 0.4 K , thus revealing the growth of magnetic correlations. This result demonstrates that CeNi_2Ge_2 is very closely located to the AFM QCP. On the other hand, at temperatures lower than $T_{\text{FL}} = 0.4\text{ K}$, $1/T_1T$ is constant; this indicates the formation of the Fermi-liquid state. The development of magnetic correlations is corroborated by the recent inelastic neutron-diffraction measurements on a single crystal of CeNi_2Ge_2 , these measurements have shown the presence of spin fluctuations with multiple q structures.¹⁵ The result for the annealed sample in the inset of Fig. 4 are almost the same as that of the as-grown sample above 0.1 K .

For the as-grown sample, as shown in Fig. 4, a remarkable finding in the Fermi-liquid regime is that the $1/T_1T$ at $H = 0$ slightly decreases below $T_c^{\text{NQR}} = 0.1\text{ K}$. Note that this temperature is lower than $T_c^{\text{onset}} = 0.2\text{ K}$ below which the

resistance begins to decrease. In order to confirm whether this decrease in $1/T_1T$ is associated with the onset of superconductivity, $1/T_1T$ was measured under external fields of $H = 0.03$ and 0.1 T , as shown by the solid triangles and squares in the figure, respectively. The application of such tiny fields causes $1/T_1T$ to remain constant down to $T = 0.07$ and 0.04 K at $H = 0.03$ and 0.1 T , respectively. This result possibly provides evidence for the onset of superconductivity at $T_c^{\text{NQR}} = 0.1$ and 0.07 K at $H = 0$ and 0.03 T , respectively. Since $1/T_1T$ indicates a power-law like dependence without a coherence peak just below T_c , the origin of superconductivity in CeNi_2Ge_2 seems to be unconventional.

Notably, as shown in the inset of Fig. 4, $1/T_1T = \text{const}$ behavior is observed down to 0.04 K for the annealed sample. Although the sample quality is improved by annealing, this SC anomaly in $1/T_1T$ as well as resistance disappears (see the inset of Fig. 1). This is possibly because a slight unconventional superconductivity in CeNi_2Ge_2 is observed in the heavy Fermi-liquid state in the close vicinity of the AFM QCP. As a result, the annealed sample seems to be apart from the SC QCP.

In this context, it is likely that CeNi_2Ge_2 is closely located to the SC QCP. This is reinforced by the comparison of $1/T_1T$ for CeNi_2Ge_2 with that for pressure-induced unconventional superconductivity in CeIn_3 above P_c .^{16,17} Figure 5 shows the T dependences of $1/T_1T$ of the as-grown sample and CeIn_3 at $P = 2.65\text{ GPa}$ ($T_c = 0.095\text{ K}$).¹⁶ The values of $1/T_1T$ and T_c are normalized by the values of $1/T_1T$ at T_c and T_c , respectively. In CeIn_3 , above $P_c = 2.45\text{ GPa}$, unconventional superconductivity is induced in the heavy Fermi-liquid state.¹⁷ Note that the superconductivity of CeIn_3 under $P = 2.65\text{ GPa}$ is revealed by the observations of zero resistance and SC diamagnetism.¹⁶ A smaller reduction in $1/T_1T$ for CeNi_2Ge_2 than for CeIn_3 below T_c could be attributed to the fact that the resistance of the as-grown sample does not become zero. These results are consistent

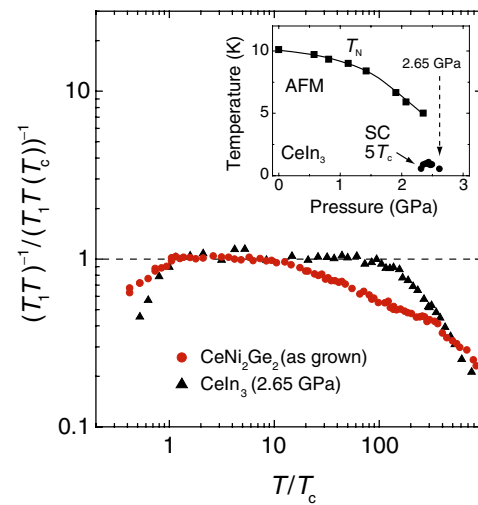


Fig. 5. (Color online) Temperature dependences of $1/T_1T$ of the as-grown sample of CeNi_2Ge_2 (solid circle) and CeIn_3 under a pressure of 2.65 GPa (solid triangle). The values of $1/T_1T$ and T_c are normalized by the values of $1/T_1T$ at T_c and T_c , respectively. Dotted line indicates a $T_1T = \text{const}$ law. The inset shows a pressure-temperature phase diagram of antiferromagnetism and superconductivity in CeIn_3 .^{16,17} The dotted arrow corresponds to $P = 2.65\text{ GPa}$.

with the fact that bulk superconductivity does not emerge but the SC coherence length remains finite over a short-range distance due to the closeness of the QCP for the SC order. In another context, if the further increase in AFM fluctuations on cooling prevented the formation of the Fermi-liquid state in CeNi_2Ge_2 , bulk superconductivity could be expected to occur due to the strong-coupling effect as demonstrated in the literatures.^{1,18)} Thus, the onset of unconventional superconductivity in HF systems is closely related to the character of AFM spin fluctuations.

In conclusion, systematic studies of resistivity and ^{73}Ge NQR in an as-grown sample of CeNi_2Ge_2 and its annealed one have revealed the development of magnetic correlations down to 0.4 K followed by the formation of a Fermi-liquid state below $T_{\text{FL}} = 0.4$ K. This very low Fermi energy is responsible for the non-Fermi-liquid-like behaviors discussed in the literatures.⁵⁻⁷⁾ A remarkable finding is that the significant reduction in $1/T_1T$ with a drop in resistance is associated with the onset of superconductivity below $T_c = 0.1$ K, this is because the application of a tiny magnetic field causes $1/T_1T$ to remain constant without a reduction of T_c below 0.1 K. These results are due to the emergence of the unconventional SC fluctuations in association with the SC QCP. This is because zero resistance is not observed. As a result, these results are consistent with the fact that bulk superconductivity does not emerge but the SC coherence length remains finite over a short-range distance due to the closeness to the SC QCP. We hope that the present works on CeNi_2Ge_2 will shed new light on the novel SC state in the heavy-Fermion compound CeNi_2Ge_2 , which is in close proximity to the AFM QCP.

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