Low-temperature specific heat and magnetic susceptibility near the pressure-induced quantum phase transition in Ce$_7$Ni$_3$

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(Received 20 May 1998)

The pressure-induced magnetic-nonmagnetic transition in a stoichiometric compound Ce$_7$Ni$_3$ was investigated using measurements of the specific heat $C$ and the magnetic susceptibility $\chi$ on single crystals down to 0.07 K. The results show that the Néel temperature $T_N$ decreases linearly with increasing pressure, and vanishes at $P_c=0.39$ GPa. At 0.36 GPa $< P_c$, the $C/T$ curve deviates strongly from $-\ln{T}$ dependence below 0.5 K, and exhibits a broad maximum around 0.15 K. At 0.43 GPa $> P_c$, while, on the other hand, a $T$-independent behavior appears below 0.2 K. These findings indicate that the $-\ln{T}$ dependence observed near $P_c$ between 0.5 and 6 K is a crossover phenomenon to a Fermi-liquid ground state. However, the continuous increase of $\chi$ down to 0.09 K at 0.43 GPa is at variance with conventional Fermi-liquid theory.

I. INTRODUCTION

In recent years, non-Fermi level (NFL) behavior in heavy-fermion alloys and compounds has received much attention. Anomalous temperature dependences of the specific heat $C$, magnetic susceptibility $\chi$, and electrical resistivity $\rho$ have been found: $C/T \propto -\ln{T}$, $\chi \propto (1 - T^{1/2})$, and $\rho \propto T$. This anomalous behavior has been attributed to distinct microscopic origins in different materials. A two-channel quadrupolar Kondo effect has been proposed to describe the NFL behavior in U$_{0.2}$Y$_{0.8}$Pd$_3$. A distribution of Kondo temperatures $T_K$ due to the disorder in UC$_{0.7-x}$Pd$_x$ ($x=1.0$ and 1.5), reproduced the anomalous temperature dependence of the specific heat and susceptibility above 0.3 K. However a spin-glass transition was found for UCu$_4$Pd at lower temperatures. The self-consistent renormalization (SCR) theory of spin fluctuations has been applied to describe the specific heat and resistivity of Ce$_{1-x}$La$_x$Ru$_2$Si$_2$ near the magnetic instability. An antiferromagnetic phase transition suppressed to $T=0$, i.e., a quantum phase transition, has been considered as the origin of the NFL behavior in some alloys, notably CeCu$_{0.7-x}$Au$_x$ (Ref. 6) and CePtSi$_{1-x}$Ge$_x$. Suppression of antiferromagnetism in CeCu$_{0.7}$Au$_{0.3}$ has also been realized by applying pressure. More recently, NFL behavior has been found even in chemically ordered compounds CeNi$_2$Ge$_2$, CeCu$_{0.5}$Si$_2$ (Refs. 9 and 10), and Ce$_2$Ni$_3$. For Ce$_7$Ni$_3$, Sereni et al. reported that an antiferromagnetically ordered state below $T_N=1.8$ K coexists with a heavy-fermion state ($\gamma=1.3$ J/K$^2$ mol Ce). This compound crystallizes in the hexagonal Th$_2$Fe$_3$-type structure and hence shows a uniaxial magnetic anisotropy. The magnetization curve for B|c at 1.4 K exhibits a metamagnetic transition at 0.2 T. The antiferromagnetism is suppressed under pressure and vanishes around 0.4 GPa, where NFL behavior appears in both the specific heat and magnetic susceptibility in the temperature range between 6 and 0.5 K. This behavior is not expected to arise from a wide distribution of Kondo temperatures $T_K$, because Ce$_7$Ni$_3$ has a chemically ordered crystal structure. However, the Ce ions at the three non-equivalent sites in Ce$_7$Ni$_3$ might have a different $T_K$. A two-channel quadrupolar Kondo effect is also unlikely due to the trigonal and monoclinic symmetry of the Ce sites in this compound. Hence, only a quantum phase transition seems to be left to explain the NFL behavior of Ce$_7$Ni$_3$. In the previous work, we have shown that the temperature dependence of $C/T$ between 5 and 0.5 K at pressures above 0.4 GPa is reproduced well by SCR theory. It is important to examine whether the $-\ln{T}$ dependence of $C/T$ holds to lower temperature or $C/T$ saturates to a constant value as is predicted by the SCR theory for three-dimensional antiferromagnets. In this paper, we report the results of the measurements of $C$ and $\chi$ down to 0.07 K for single crystals of Ce$_7$Ni$_3$ under various pressures.

II. EXPERIMENTAL PROCEDURE

Single crystals of Ce$_7$Ni$_3$ were grown by a Czochralski method using a hot tungsten crucible in an rf induction furnace. As starting materials, we used high-purity Ce and Ni metals produced by Ames Laboratory and Johnson Matthey Ltd., respectively. The crystal orientation was determined by the backscattering Laue method.

The magnetization under pressures up to 1.2 GPa was measured by an extraction method with a clamp-type piston cylinder pressure cell at ISSP, University of Tokyo. The pressure cell was immersed in liquid $^3$He and cooled down...
to 0.5 K. The detailed technique of the magnetization measurement is described elsewhere.\textsuperscript{16}

The measurements of the heat capacity $C$ and the ac susceptibility $\chi_{ac}$ under pressure have been done down to 0.07 K in a $^3$He-$^4$He dilution refrigerator at the University of Karlsruhe. For these measurements, we used a standard heat-pulse and an ac mutual inductance method, respectively. A single-crystalline sample of $\sim$100 mg with a cylindrical shape along the $c$ axis was put into the Cu-Be pressure cell. We used a methanol-ethanol mixture as a pressure transmitting medium. The coils for the ac susceptibility measurements were mounted outside of the pressure cell, and were also used to measure the superconducting transition of a small Sn piece to determine the pressure. The frequency and amplitude of ac field were 129.5 Hz and less than 0.02 mT, respectively. The contributions of the pressure cell to $C$ and $\chi_{ac}$ were determined in separate measurements without the sample and subtracted from the raw data. For the ac susceptibility the $T$ dependence of the pressure cell between 0.09 and 3 K is small compared to that of the sample for most pressures. For $P \leq 0.35$ GPa, the magnetization curve is strongly depressed within increasing pressure, and the value of 0.55 T is only 0.011 $\mu_B$/Ce for $P = 1.2$ GPa. Likewise, $M(B||a)$ decreases with pressure, albeit at a slower rate. The ratio $M(B||c)/M(B||a)$ at 0.55 T reaches a maximum of 7.7 at 0.4 GPa and decreases to 3.8 at 1.2 GPa. Thus, strong anisotropy survives in the paramagnetic state.

The isothermal magnetization curves $M(B)$ at 0.5 K for $B||c$ and $B||a$ are shown in Fig. 1. At $P = 0$, a sharp metamagnetic transition occurs at 0.18 T only for $B||c$, which is in agreement with the previous observation.\textsuperscript{15} With increasing pressure up to 0.25 GPa, the transition field $B_c$ decreases at the rate of $dB_c/dP = -0.71$ GPa, and for 0.35 GPa, no metamagnetic transition was observed at 0.5 K. For $P \geq 0.35$ GPa, the magnetization curve is strongly depressed within increasing pressure, and the value of $M$ is only 0.011 $\mu_B$/Ce for $P = 1.2$ GPa. Likewise, $M(B||a)$ decreases with pressure, albeit at a slower rate. The ratio $M(B||c)/M(B||a)$ at 0.55 T reaches a maximum of 7.7 at 0.4 GPa and decreases to 3.8 at 1.2 GPa. Thus, strong anisotropy survives in the paramagnetic state.

The magnetic susceptibility $\chi_{dc} = M/B$ was determined in the low-field range where $M$ is proportional to $B$. For $B||c$ and $P \leq 0.25$ GPa, the magnitude of $B$ was chosen in the range below $B_c$, and for $P \geq 0.35$ GPa, $B$ was kept at 0.05 T. Figure 2 shows the temperature dependence of $\chi_{dc}$. For $B||c$, $\chi_{dc}$ at $P = 0$ exhibits a peak at 1.9 K due to the antiferromagnetic transition. By contrast, $\chi_{dc}(B||a)$ shows no anomaly at $T_N$ and the temperature dependence levels off below 0.7 K. The previous specific heat and ac susceptibility data for $P$
=0 suggested the presence of another magnetic transition at 0.6 K.\textsuperscript{13} The saturated behavior in $\chi_{dc}(B∥a)$ might be due to the onset of this transition. With increasing pressure up to 0.25 GPa, the peak height in $\chi_{dc}$ decreases strongly. At 1.2 GPa, $\chi_{dc}$ for both $B∥c$ and $B∥a$ shows Pauli paramagnetic behavior with 0.01 and 0.003 emu/mol Ce, respectively.

The significant change in the magnetic susceptibility near the critical pressure has been further studied by the measurement of ac susceptibility $\chi_{ac}$ down to 0.07 K. The temperature dependences of $\chi_{ac}$ for $B∥c$ under various pressures are shown in Fig. 3, together with the data of $\chi_{ac}$ at 0.25 GPa which corroborates the results for $\chi_{ac}(T)$. For 0.36 GPa, $\chi_{ac}(T)$ exhibits a maximum at 0.096 K with the maximum value larger than that for 0.25 GPa. For 0.43 GPa, $\chi_{ac}(T)$ is much smaller and it gradually increases with decreasing temperature down to 0.09 K without any peak.

Figure 4 shows the magnetic contribution to the specific heat divided by temperature, $C_{m}/T$. The specific heat for La$_7$Ni$_3$ was subtracted as an estimate for the nonmagnetic contribution, which is less than 3% of $C/T$ for Ce$_7$Ni$_3$ at 1 K.\textsuperscript{11,12} The two magnetic transitions manifest themselves in the two maxima in the zero-pressure data at 1.8 and 0.6 K. At 0.11 GPa, the maximum at the higher temperature shifts to 1.2 K, whereas the other one disappears. At 0.35 GPa, $C/T$ exhibits only a broad maximum centered at 0.2 K, which further broadens for 0.36 GPa. This broad maximum around 0.15 K can be ascribed to some type of magnetic transition because $\chi_{ac}(T)$ has a peak at 0.096 K as shown in Fig. 3. The behavior in both $C_{m}/T$ and $\chi_{ac}$ is reminiscent of a spin-glass transition.\textsuperscript{17} However, because a neutron diffraction study confirmed the chemically ordered structure of Th$_7$Fe$_3$ type,\textsuperscript{18} the magnetic transition of this compound at 0.36 GPa appears unlikely to be a spin-glass transition. For 0.43 GPa, $C_{m}/T$ levels off to a temperature independent value of 0.68 J/K$^2$ mol Ce below 0.2 K, indicating the recovery of the Fermi-liquid state with strongly enhanced effective electron mass. However, $C_{m}/T$ exhibits a shallow maximum around 0.4 K. Since no anomaly appears in $\chi_{ac}(T)$ there, this maximum cannot be attributed to a magnetic transition.

The above results of $C$, $\chi_{dc}$, and $\chi_{ac}$ allow us to determine the pressure dependence of $T_N$ as shown in Fig. 5. We took the temperature of the maximum of $d(\chi T)/dT$ as $T_N$. For the specific heat, the position of the maximum of $C_m(T)$ is practically indistinguishable from those of $C_{m}/T$ for $P ≈ 0.31$ GPa. For larger $P$, a distinctive feature in $C_m(T)$ does not occur. However, a maximum in $C_{m}/T$ is still observed up to 0.36 GPa. We therefore tentatively took these temperatures as an indication of magnetic order. With increasing pressure $P$, $T_N$ decreases linearly and the relation $T_N = 1.81 (K) - 4.65P$ (K/GPa) yields the critical pressure $P_c = 0.39$ GPa where $T_N → 0$. The dependence of $T_N$ near the quantum critical point was investigated theoretically by Millis using a renormalization group (RG) theory.\textsuperscript{19} For an effective dimension $d = 3$, the RG results confirm those of the self-consistent renormalization (SCR) theory of spin
fluctuations. The RG theory predicts that \( T_N \) varies as \( |\delta - \delta_c|^{2/(z+1)} \) where \( \delta \) and \( z \) are a relevant scaling variable and dynamical exponent, respectively. It was assumed that \( \delta \) can be tuned by pressure, i.e., \( |\delta - \delta_c| \approx |P - P_c| \). For the antiferromagnetic case with \( z = 2 \), we expect that \( T_N \) varies as \((P_c - P)^{2} \). However, in certain systems, \( \text{CeCu}_5\text{Au}_{0.3} \) (Ref. 8) and \( \text{CePd}_2\text{Si}_2 \) (Ref. 20) the variation of \( T_N \) was found to be linear in \((P_c - P)\) as observed in the present case. This point requires further study. We note that \( d = 2 \) for the critical fluctuations leads to a linear \( T_N \) dependence on \( P \).\(^{1,21}\)

We now discuss the specific heat of \( \text{Ce}_7\text{Ni}_3 \) in the vicinity of \( P_c \). As mentioned above, the \( C_m/T \) curve at 0.36 GPa deviates strongly from the \( -\ln T \) dependence below 0.5 K and exhibits a broad maximum. On the other hand, for \( P > 0.43 \) GPa, i.e., not far from the critical pressure \( P_c = 0.39 \) GPa, \( C_m/T \) is practically constant between 0.07 and 0.5 K, compatible with Fermi-liquid behavior. This behavior is in marked contrast to that of \( \text{CeCu}_{6-x}\text{Au}_x \) under pressure. For \( x = 0.2 \) and 0.3, an appreciable pressure range near \( P_c \) exists where \( C/T \) exhibits the characteristic \( -\ln T \) dependence.\(^{8}\) For \( \text{Ce}_7\text{Ni}_3 \), however, it is apparent from Fig. 4 that even for \( P = P_c \), \( C_m/T \) is unlikely to show a \( -\ln T \) dependence over a large temperature range as it might be bounded by the two curves for \( P = 0.36 \) and 0.43 GPa.

We now turn to the shallow maximum in \( C_m/T \) around 0.4 K observed at 0.43 GPa. Recently, similar behavior in the specific heat of \( \text{CeNi}_2\text{Ge}_2 \) under magnetic field has been reported.\(^{22}\) For zero field, \( C/T \) follows the form of \( C/T = \gamma - \beta T^{1/2} \). In fields \( B > 4 \) T, \( C/T \) shows a broad maximum at around 1 K, below which \( C/T \) becomes independent of temperature. This maximum of \( C/T \) can be modeled by assuming a density of states (DOS) at the Fermi energy \( E_F \), i.e., \( D(e) = \Delta_0 - D_1 |e|^{1/2} \). This form of \( D(e) \) is consistent with the theory which takes the effect of spin fluctuations on the self-energy of quasiparticles into consideration.\(^{23}\) By using this model, we could not reproduce the data of \( C_m/T \) at \( P = 0.43 \) GPa for \( \text{Ce}_7\text{Ni}_3 \). A better fit was obtained by shifting the Fermi level above the peak of the DOS by 1.9 K, i.e., \( D(e) = \Delta_0 - D_1 |e - e_0|^{1/2} \), where \( e_F - e_0 = 1.9 \) K.

Although the recovery of a Fermi-liquid state at low temperatures below 0.2 K for \( P = 0.43 \) GPa is suggested by the \( T \)-independent behavior of \( C_m/T \), the continuous increase of \( \chi_{dc} \) down to 0.09 K as shown in Fig. 3 is at variance with this interpretation. Such an increase cannot be ascribed to the effect of magnetic impurities in either the sample or the pressure cell, because \( \chi_{dc} \) for \( P = 0.11 \) GPa is constant down to 0.2 K after subtraction of the susceptibility of the empty pressure cell from the raw data. Figure 6 displays the double logarithmic plot of \( \chi_{dc} \) vs \( T \) above 0.35 GPa. For \( B || c \), \( \chi_{dc}(T) \) at 0.4 GPa does not follow a simple power law, and at 0.5 and 0.6 GPa the temperature dependence of \( \chi_{dc} \) weakens towards low temperatures, suggesting the recovery of Fermi-liquid behavior. Interestingly, as shown in the lower part of Fig. 6, \( \chi_{dc}(T) \) for \( B || a \) at both \( P = 0.4 \) and 0.6 GPa also increases weakly with \( \chi_{dc} \propto T^{-0.2} \) in the whole temperature range from 4 to 0.5 K.

In conclusion, we found that the \( -\ln T \) dependence of \( C_m/T \) of \( \text{Ce}_7\text{Ni}_3 \) just above \( P_c = 0.39 \) GPa changes to a \( T \)-independent behavior, i.e., normal Fermi-liquid behavior at lower temperatures below 0.2 K. However, at \( P = 0.43 \) GPa, both the broad maximum of \( C_m/T \) at 0.4 K and the continuous increase in \( \chi(T) \) are not consistent with a conventional Fermi-liquid theory. These facts suggest that both \( C(T) \) and \( \chi(T) \) near \( P_c \) are strongly affected by spin fluctuations. In order to investigate the character of the spin fluctuations, neutron scattering experiments under pressure are in progress.

**ACKNOWLEDGMENTS**

We thank N. Watanabe and Y. Echizen for their help in the crystal growth. Magnetic measurements under pressure were carried out by the joint research in the Institute for Solid State Physics, the University of Tokyo. This work was financially supported in part by a Grant-in-Aid for International Joint Research Program from Ministry of Education, Science and Culture of Japan.

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