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Transition from magnetic to nonmagnetic ground state in a heavy-fermion compound Ce_7Ni_3 under high pressure

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The electrical resistivity and ac magnetic susceptibility of the heavy-fermion compound Ce_7Ni_3 were measured in the temperature range from 0.4 to 300 K and in the pressure range up to 1.5 GPa. The Néel temperature of 1.9 K for antiferromagnetic transition at ambient pressure decreases with increasing pressure and vanishes at about 0.33 GPa. The magnetic resistivity, $\rho_m = \rho(Ce_7Ni_3)$-$\rho(La_7Ni_3)$, decreases steeply with pressure, and above 0.66 GPa, $\rho_m(T)$ can be described by the expression $\rho_m(T) = \rho_m(0) + AT^2$. The coefficient A decreases and the temperature range in which the T^2 dependence is held becomes wider with increasing pressure. The electronic Grüneisen parameter for the Kondo temperature T_K, $-\partial \ln T_K / \partial \ln V$, is evaluated to be 132 from the pressure dependence of A. This value is larger than that of typical heavy-fermion compounds. The results are discussed in relation to the competition between the magnetic interaction and the Kondo interaction in Ce_7Ni_3. [S0163-1829(96)03326-7]

I. INTRODUCTION

Many cerium-based compounds order magnetically at low temperatures, although the Kondo effect at each Ce site is expected to form a nonmagnetic ground state. According to Doniach's phase diagram[1] for the Kondo lattice, the Néel temperature T_N, Kondo temperature T_K, and the characteristic temperature T_{RKKY} of the RKKY interaction, are described by a common parameter $|JN(E_F)|$, where J is the exchange coupling between the $4f$ and conduction electrons and $N(E_F)$ is the conduction-band density of states. In the region of small $|JN(E_F)|$, T_K is lower than T_{RKKY} and the compound undergoes an antiferromagnetic transition. With increasing $|JN(E_F)|$, T_K exceeds T_{RKKY} and the magnetic order is suppressed. When $|JN(E_F)|$ exceeds the critical value $|JN(E_F)|_c$, the ground state becomes that of a strongly correlated Fermi liquid. With further increasing $|JN(E_F)|$, the system becomes an intermediate valence state.

For magnetically ordered Ce compounds in the region $|JN(E_F)| < |JN(E_F)|_c$, pressure increases hybridization and moves the system to the larger $|JN(E_F)|$ region.[2] Indeed, pressure-induced transitions from an antiferromagnetic to nonmagnetic state have been reported for several compounds, e.g., $CeIn_3$ (Ref. 3), $CeRh_2Si_2$ (Ref. 4), and $CeCu_2Ge_2$ (Ref. 5).

Ce_7Ni_3 is a heavy-fermion compound which antiferromagnetically orders at $T_N = 1.8$ K.[6,7] In our previous works, the significant change in electronic state with pressure was found by the measurements of the temperature dependence of the electrical resistivity and specific heat.[8,9] In fact, the temperature T_m at which the magnetic resistivity exhibits a maximum increases drastically by applying pressure above 0.5 GPa.[8] This result is explained qualitatively by the increase of T_K with pressure because T_K evaluated from the specific heat above 0.5 GPa increases steeply with pressure. The electronic Grüneisen parameter Γ_e was estimated to be as large as 400 from the pressure dependence of T_K with the bulk modulus of 100 GPa.[9] These facts imply that the heavy-fermion state transforms rapidly into the intermediate valence state under pressure. From these studies, it is expected that the transition from magnetic to nonmagnetic state takes place at rather low pressure below 0.5 GPa.

In the present work, we have examined the change in both T_N and T_K of Ce_7Ni_3 with pressure around the critical value of $|JN(E_F)|_c$ in detail. We have measured the ac magnetic susceptibility χ_{ac} of a polycrystalline sample and the electrical resistivity along the c axis of a single crystal down to 0.35 K and under pressure up to 1.5 GPa. Based on these results, we discuss the competition between the Kondo effect and magnetic interaction in this compound.

II. EXPERIMENTAL PROCEDURE

Ingots of Ce_7Ni_3 and La_7Ni_3 were prepared by melting of the starting materials under a pure argon atmosphere in an arc furnace. The starting materials of Ce and La were 99.9% and Ni was 99.99% in purity. An excessive amount of Ce and La of about 1.7 at % was added to obtain single-phase samples. The alloy ingots were homogenized by annealing in vacuum at 400 °C for 7 days. By powder x-ray analysis, the Th_7Ni_3-type structure was confirmed. The lattice constants a and c of Ce_7Ni_3 were 9.936(1) and 6.314(1) Å, respectively, in good agreement with those reported.[10] A single crystal of Ce_7Ni_3 was obtained by cooling slowly the ingot on a tungsten plate in the furnace. The crystal orientation was determined by the back Laue method.

The electrical resistivity under pressure up to 1.5 GPa was

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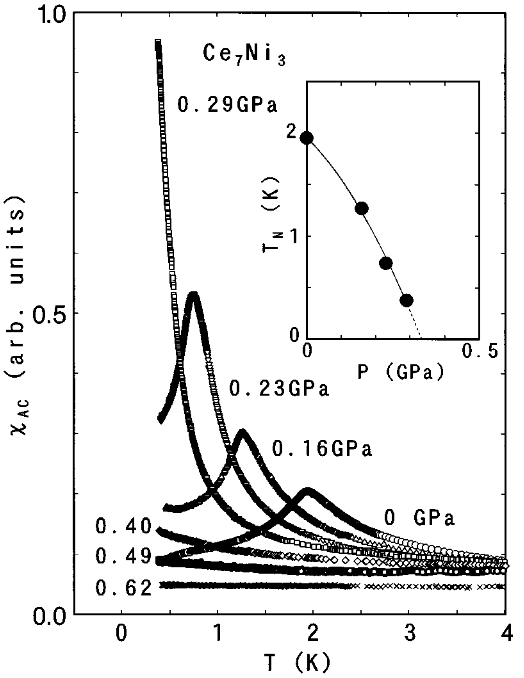

FIG. 1. Temperature dependence of ac magnetic susceptibility $\chi_{\rm ac}$ at various pressures up to 0.62 GPa. The inset shows the pressure dependence of T_N.

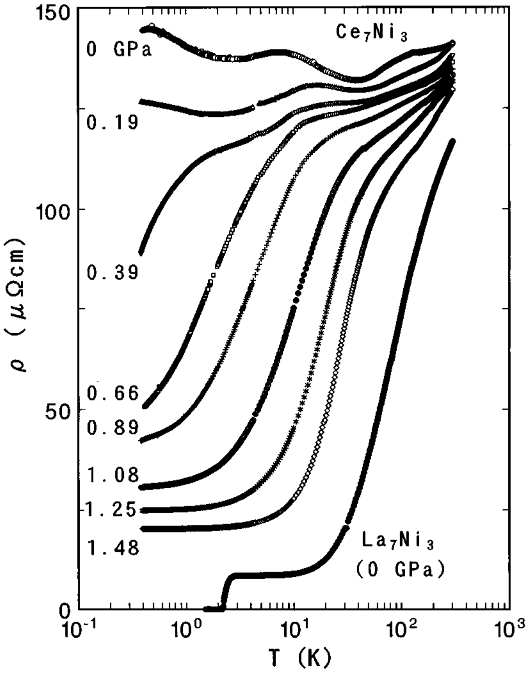

FIG. 2. Temperature dependence of the electrical resistivity measured along the c axis of the Ce$_7$Ni$_3$ single crystal at various pressures up to 1.48 GPa.

measured by a dc four-terminal method with a clamp-type piston cylinder pressure cell.[11] This pressure cell was mounted to the ^{3}He cryostat (Heliox, Oxford Instruments Ltd). The pressure was estimated with a superconducting Pb manometer.

The measurement of $\chi_{\rm ac}$ was performed by means of the Hartshorn bridge in the ranges of $0.35 \leqslant T \leqslant 4$ K and 0.1 MPa $\leqslant P \leqslant 0.62$ GPa. The frequency and magnetic field were 100 Hz and 1.8 Oe, respectively.

X-ray diffraction experiments under pressure were carried out with monchromaced Mo $K\alpha$ radiation at room temperature. The camera length was estimated from the Debye-Scherrer rings of NaCl. Quasihydrostatic pressure was generated by a diamond anvil cell using a pressure medium of silicone grease. The powdered sample mixed with NaCl powder and a ruby chip were placed in a 0.3-mm hole at the center of a stainless-steel gasket 0.5 mm in thickness. The pressure in the cell was determined by a ruby fluorescent method.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of $\chi_{\rm ac}(T)$ at various pressures up to 0.62 GPa. At ambient pressure, the maximum at 1.9 K indicates the onset of an antiferromagnetic order. Furthermore, a broad swell exists around 0.6 K, as was reported by Sereni *et al.*[12] With increasing pressure up to 0.29 GPa, T_N defined by the maximum temperature of $\chi_{\rm ac}(T)$ decreases and the value of $\chi_{\rm ac}$ at T_N increases. As shown in the inset, T_N vanishes at about $P_c = 0.33$ GPa. Above 0.4 GPa, the $\chi_{\rm ac}$ decreases strongly over the measured temperature range, and at 0.62 GPa, $\chi_{\rm ac}$ becomes almost independent of temperature. This suggests that the ground state changes into the paramagnetic state near 0.6 GPa.

Figure 2 shows the temperature dependence of electrical resistivity $\rho(T)$ along the c axis of Ce$_7$Ni$_3$ single crystal at various pressures up to 1.48 GPa. At ambient pressure, $\rho(T)$ decreases with decreasing temperature from 300 K, reaches a minimum at around 40 K, and exhibits two maxima at 8 and 0.5 K. By applying pressure $\rho(T)$ decreases over the temperature range, and eventually $\rho(T)$ approaches that of La$_7$Ni$_3$. The drop in resistivity of La$_7$Ni$_3$ at 2.1 K is due to a superconducting transition.[8]

The magnetic contribution to $\rho(T)$ from $4f$ electrons was estimated by using the relation $\rho_m = \rho({\rm Ce_7Ni_3}) - \rho({\rm La_7Ni_3})$. The value for La$_7Ni_3$ below 2.1 K was estimated by the extrapolation of $\rho(T)$ data from 10 to 3.0 K. As is shown in Fig. 3, $\rho_m(T)$ for $T \geqslant 50$ K is proportional to $-\ln T$, which is characteristic of so-called ''dense Kondo system.'' At ambient pressure, ρ_m exhibits two maxima at 8 and 0.5 K and a local minimum around 2 K. The maximum at 8 K is considered to be the onset of coherent scattering of conduction electrons from periodically arrayed Ce ions. It is noteworthy that ρ_m turns up below $T_N = 1.9$ K whereas magnetic scattering usually decreases below T_N. This fact may suggest the complex magnetic structure. The maximum at 0.5 K may be related with the anomaly at 0.6 K in $\chi_{\rm ac}(T)$.

The upturn of ρ_m disappears above 0.33 GPa, at which the magnetic order disappears. With increasing pressure further, the maximal temperature T_m increases and the maximal value $\rho_m(T_m)$ decrease. Above 0.66 GPa, $\rho_m(T)$ follows the T^2 law at low temperatures, $\rho_m(T) = \rho_m(0) + AT^2$. The $\rho_m(T) - \rho_m(0)$ above 0.66 GPa is plotted as a function of T^2 in Fig. 4, where straight lines are guides for the eyes. The temperature range in which the relation $\rho_m(T) - \rho_m(0) = AT^2$ is held becomes wider and the coefficient A decreases as pressure increases. These behaviors

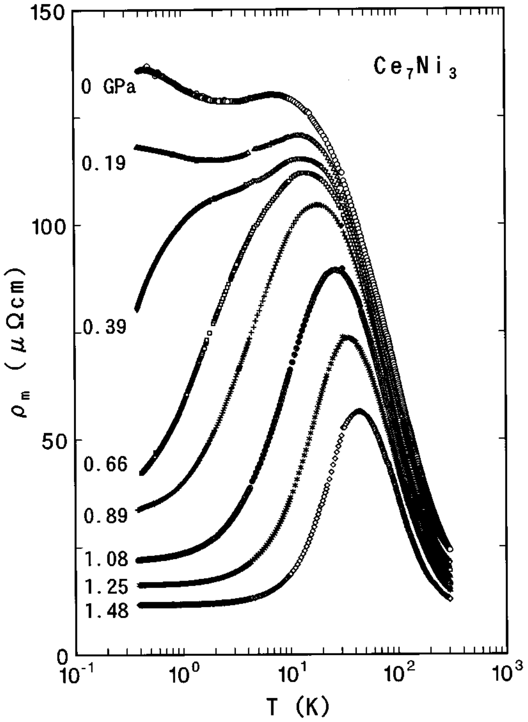

FIG. 3. The magnetic contribution ρ_m to the electrical resistivity of $\mathrm{Ce_7Ni_3}$ vs temperature at various pressures.

were observed in heavy-fermion compounds such as $\mathrm{GeInCu_2}$,[13] $\mathrm{CeCu_6}$,[14] and $\mathrm{CeCu_2Si_2}$.[15] The pressure dependence of A and T_m has been discussed on the basis of the periodic Anderson model neglecting the crystalline electric field (CEF) effect.[16] It has been shown that the Kondo temperature T_K is proportional to T_m and $A^{-1/2}$, i.e.,

$$T_K \propto T_m \propto A^{-1/2} \propto \exp\left(\frac{-1}{|JN(E_F)|}\right). \tag{1}$$

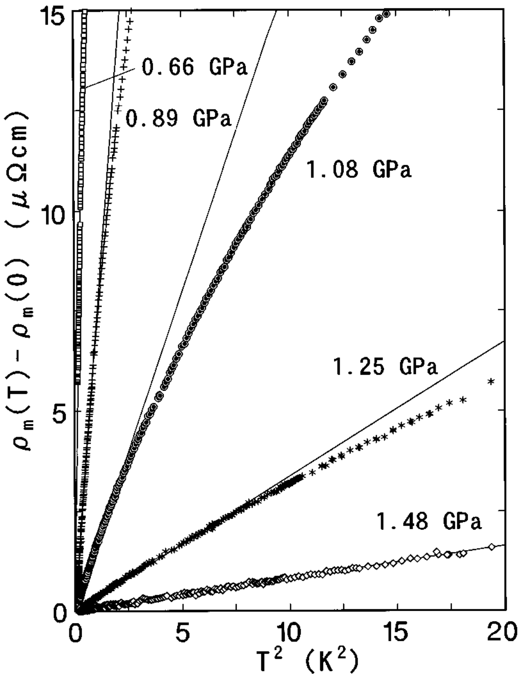

FIG. 4. T^2 dependence of $\rho_m(T) - \rho_m(0)$ at various pressures. $\rho_m(0)$ is the residual resistivity. The solid line is the straight line through the origin of the figure drawn as a guide for the eyes.

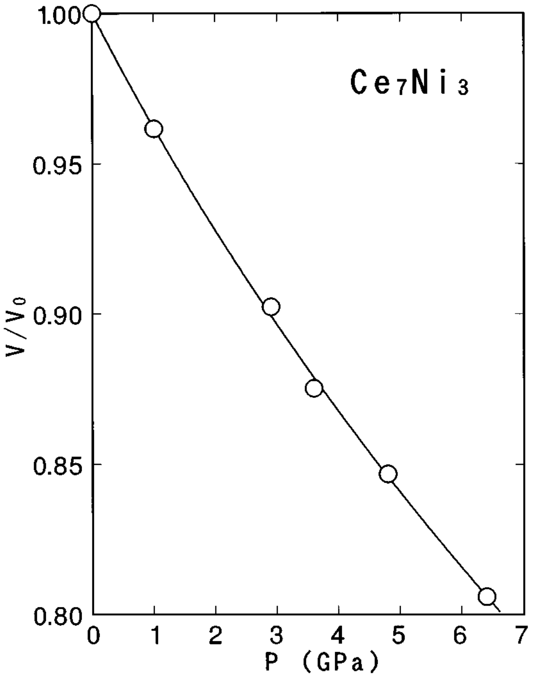

FIG. 5. Relative change of the volume V/V_0 of the $\mathrm{Ce_7Ni_3}$ as a function of pressure and fit to the Murnaghan-Birch equation.

The observed decrease of A with pressure leads to the increase of $|JN(E_F)|$.

Within the compressible Kondo model,[2] the volume dependence of $|JN(E_F)|$ is assumed as follows:

$$|JN(E_F)| = |JN(E_F)|_0 \exp\left(-q\frac{V-V_0}{V_0}\right), \tag{2}$$

where $|JN(E_F)|_0$ is the value of $|JN(E_F)|$ at ambient pressure, q is a numerical constant usually taken to be between 6 and 8, V and V_0 are the unit cell volumes at pressure P and at ambient pressure, respectively.

In $\mathrm{Ce_7Ni_3}$, the T^2 dependence of $\rho_m(T)$ was observed above 0.66 GPa. Therefore, for the discussion on the pressure dependence of A, we use the following equation obtained from Eqs. (1) and (2):

$$\begin{aligned} -\frac{1}{2}\ln\frac{A(P)}{A(0.66)} &= \ln\frac{T_m(P)}{T_m(0.66)} \\ &= \frac{1}{|JN(E_F)|_0}\left\{\exp\left(q\frac{V_{0.66}-V_0}{V_0}\right)\right. \\ &\quad \left. -\exp\left(q\frac{V-V_0}{V_0}\right)\right\}, \end{aligned} \tag{3}$$

where $A(0.66)$, $T_m(0.66)$, and $V_{0.66}$ are the values of A, T_m, and V at $P = 0.66$ GPa.

The evaluation of the pressure dependence of A and T_m by Eq. (3) requires the knowledge of $(V-V_0)/V_0$. Figure 5 shows the relative change of the room-temperature unit-cell volume V/V_0 as a function of pressure, which was determined from x-ray-diffraction measurements. The linear decrease of V/V_0 with pressure can be accounted for by

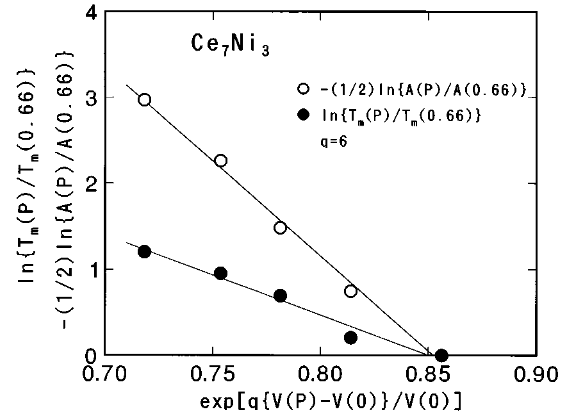

FIG. 6. $-(1/2)\ln[A(P)/A(0.66)]$ and $\ln[T_m(P)/T_m(0.66)]$ vs $\exp[q(V-V_0)/V_0]$ of $\mathrm{Ce_7Ni_3}$ assuming $q=6$.

Murnaghan-Birch's equation.[17] The results of a least-squares fit give the bulk modulus $B_0=24.6$ GPa and its volume derivative $d\ln B_0/d\ln V=2.1$. To trace the P dependence predicted by Eq. (3), both $(-1/2)\ln[A(P)/A(0.66)]$ and $\ln[T_m(P)/T_m(0.66)]$ are plotted in Fig. 6 as a function of $\exp[q(V-V_0)/V_0]$ assuming $q=6$. This figure indicates the linear dependence of both values on the parameter $\exp[q(V-V_0)/V_0]$. The slopes of $A(P)$ and $T_m(P)$ yield the values 4.5×10^{-2} and 11×10^{-2}, respectively, for $|JN(E_F)|_0$. The former value is about half those for typical heavy-fermion compounds $\mathrm{CeCu_6}$ (9.1×10^{-2}) and $\mathrm{CeInCu_2}$ (8.1×10^{-2}) (Ref. 18) estimated by the similar method. We now discuss the difference in the values of $|JN(E_F)|_0$ estimated from $A(P)$ and $T_m(P)$. This value is related with that of the volume dependence of T_K from Eqs. (1) and (2). In $\mathrm{Ce_7Ni_3}$, the sixfold-degenerate states of the $4f$ electron of Ce^{3+} at low symmetric site may split into three Kramers doublets. It is known that T_m is known to be strongly influenced by the low-lying CEF state at the excitation energy of Δ. According to Cornut's theory[19] taking account of the CEF effect on the Kondo lattice, T_m increases with increasing Δ. Since Δ itself depends on the cell volume, it is hard to estimate the pressure dependence of T_K solely from the result of $T_m(P)$. On the other hand, the T^2 coefficient A is related to the Sommerfeld coefficient γ $(\propto T_K^{-1})$ as $A\propto\gamma^2$ for many Ce and U compounds.[20] This fact suggests that the value of T_K can be estimated from the value of A independently of the CEF effect.

The electronic Grüneisen parameter Γ_e for the Kondo temperature T_K is described as follows:

$$\Gamma_e=-\frac{\partial\ln T_K}{\partial\ln V}. \tag{4}$$

From Eqs. (1) and (4), we obtain

$$\Gamma_e=\frac{1}{2}\frac{\partial\ln A}{\partial\ln V} =\frac{q}{|JN(E_F)|_0}\left(\frac{V}{V_0}\right)\exp\left(q\frac{V-V_0}{V_0}\right). \tag{5}$$

Equation (5) indicates that the value of Γ_e is inversely proportional to $|JN(E_F)|_0$ and depends on volume. Assuming $q=6$, Γ_e ($P=0$, i.e., $V=V_0$) is estimated to be 132, which is larger than those of $\mathrm{CeCu_6}$ (70–80) (Ref. 21) and $\mathrm{CeCu_2Si_2}$ (22-80) (Ref. 21). This fact is related with the small value of $|JN(E_F)|_0$ in $\mathrm{Ce_7Ni_3}$ compared to those of $\mathrm{CeCu_6}$ and $\mathrm{CeCu_2Si_2}$. From the specific-heat measurement at high pressure,[9] we have estimated the value of $\partial\ln T_K/\partial P$ to be 4.0 GPa^{-1}. By using $B_0=24.6$ GPa in Eq. (4), Γ_e is estimated to be 100, which value agrees with that obtained in the present work.

We now discuss the competition between the Kondo and magnetic interactions in $\mathrm{Ce_7Ni_3}$. From the pressure dependence of low-temperature specific heat, T_K at 0.66 GPa was estimated to be 44 K.[9] By substituting $T_K(0.66)=44$ K, $|JN(E_F)|_0=4.5\times10^{-2}$ and $q=6$ in Eqs. (1) and (3), the value of $T_K(0)$ is estimated to be 1.9 K. The fact that the value of T_K is in accord with $T_N=1.9$ K implies that the Kondo interaction and the RKKY interaction balance each other at ambient pressure.

In $\mathrm{Ce_7Ni_3}$, the critical pressure P_c is 0.33 GPa where the transition occurs from antiferromagnetically ordered state to the nonmagnetic state. This value is much smaller than that of the usual Ce compounds with antiferromagnetic order at ambient pressure such as $\mathrm{CeIn_3}$ ($P_c=3.5$ GPa),[3] $\mathrm{CeAl_2}$ ($P_c=4.0$ GPa),[3] and $\mathrm{CeCu_2Ge_2}$ ($P_c=7.5$ GPa).[5] This fact indicates that for $\mathrm{Ce_7Ni_3}$ the value of $|JN(E_F)|_0$ is close to a critical value of $|JN(E_F)|_c$ which corresponds to the value of $|JN(E_F)|$ at the transition to the nonmagnetic state.

Recently, Continentino[22] analyzed the pressure dependence of electrical resistivity, specific heat, and susceptibility of heavy-fermion systems by using a quantum scaling theory. According to his result, if the $|JN(E_F)|_0$ is close to $|JN(E_F)|_c$, Γ_e becomes very large as $1/[1-|JN(E_F)|_c/|JN(E_F)|_0]$. The critical value of $|JN(E_F)|_c$ for $\mathrm{Ce_7Ni_3}$ is obtained to be 4.9×10^{-2} from Eq. (3). The large value of Γ_e for $\mathrm{Ce_7Ni_3}$ may be due to the fact that the value of $|JN(E_F)|_0$ is close to $|JN(E_F)|_c$.

In conclusion, we have found that for $\mathrm{Ce_7Ni_3}$ the transition from a magnetic to nonmagnetic state takes place at 0.33 GPa and the electronic Grüneisen parameter Γ_e for T_K at the nonmagnetic state is very large in comparison with typical heavy-fermion compounds. Furthermore, from the volume dependence of T_N shown in the inset of Fig. 1, $\partial\ln T_N/\partial\ln V$ $(=\Gamma_N)$ at ambient pressure is found to be 42. The value is greater than that of Ce compounds with similar values of T_N such as $\mathrm{CeIn_3}$ $(\Gamma_N=2)$ and $\mathrm{CeAl_2}$ $(\Gamma_N=12)$.[3] The Grüneisen parameter Γ_N for $\mathrm{Ce_7Ni_3}$ becomes about 700 around at 0.3 GPa. The large Grüneisen parameter may be the combined effects of the electronic state being the close to the nonmagnetic transition and of the critical balance between the Kondo and RKKY interaction at ambient pressure.

ACKNOWLEDGMENTS

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