Random magnetic moments and spin-glass-like behaviors in the heavy-fermion compound $CeNi_2Sn_2$

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We have studied the magnetic, electric, and thermal properties of $CeNi_2Sn_2$. The zero-field-cooled susceptibility $\chi_{ZFC}(T)$ deviates from the field-cooled susceptibility $\chi_{FC}(T)$ below 3 K. Both real (χ') and imaginary (χ'') components of the ac susceptibility exhibit pronounced maxima at ~4 and ~5 K. At 2 K, the magnetization $M(H)$ clearly exhibits hysteresis. The zero-field cooled-magnetization $M_{ZFC}(t)$ is frozen at 2 K in a 0.005-T field with an enormous time constant of 917 sec. In 0.005 T, zero-field-cooled resistivity $\rho_{ZFC}(T)$ starts to deviate from field-cooled resistivity $\rho_{FC}(T)$ at ~8 K, and both $\rho_{ZFC}(T)$ and $\rho_{FC}(T)$ rapidly decrease as the temperature is below 5 K. These behaviors suggest a spin-glass phase transition at $T_f \sim 3$ K for $CeNi_2Sn_2$. The coefficient of the term linear in temperature γ, in the specific heat of $CeNi_2Sn_2$ between 30 and 40 K, is 112 $mJ\,mol^{-1}\,K^{-2}$, which is much larger than those of normal metals. $CeNi_2Sn_2$ is a true heavy fermion with spin-glass-like behavior. In a 10-T field, the temperature dependence of C_m/T exhibits a peak at ~5 K. The easiest interpretation for this behavior is that, in a high magnetic field, there is a field-induced ferromagnetic phase transition at ~5 K.

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I. INTRODUCTION

Rare-earth-metal ternary silicides with the $ThCr_2Si_2$ or $CaBe_2Ge_2$ tetragonal structure exhibit a rich variety of physical phenomena, such as heavy-fermion behavior, mixed valence, and superconductivity. $CeNi_2Sn_2$ crystallizes with the $CaBe_2Ge_2$ tetragonal structure and was first studied by Skolozdra *et al.*[1] Several groups[2–5] have measured the magnetic properties, resistivity, and specific heat of $CeNi_2Sn_2$, and they classify this compound to be a heavy-fermion system with an electronic specific-heat coefficient γ reaching 0.6 $J\,mol^{-1}\,K^{-2}$.[5] Besides, $CeNi_2Sn_2$ is in an antiferromagnetic order below $T_N \sim 1.8$ K.

A large negative magnetoresistance of $CeNi_2Sn_2$ was observed in the vicinity of 2 K.[6] Following the approach proposed by Abrikosov to calculate the resistivity in weakly spin-correlated Kondo-like system, Gridin *et al.*[6] were able to fit the temperature and field dependences of $CeNi_2Sn_2$ successfully, which suggests that there are weakly correlated Kondo-like random magnetic moments in $CeNi_2Sn_2$. Frequently, correlated magnetic moments might form magnetic clusters. A tiny ferromagnetic component ($0.02\mu_B$ per formula unit[7]) and a huge anisotropy of susceptibility[5] also suggest the existence of magnetic clusters in $CeNi_2Sn_2$.

It is also known that two allotropic forms exist for $CeNi_2Sn_2$.[8] The structure instability of $CeNi_2Sn_2$ will produce random magnetic moments. At low temperature, these random magnetic moments might correlate to form magnetic clusters. The magnetic clusters are the building blocks out of which the spin glass is established. If magnetic clusters are linked, $CeNi_2Sn_2$ will be in a short-range spin-glass-type order. Therefore, $CeNi_2Sn_2$ is suitable for studying the magnetic order from paramagnetic random magnetic moments, magnetic clusters, short-range spin-glass-type to long-range antiferromagnetic order. In this paper we report the spin-glass-like behaviors of magnetic, electric, and thermal measurements for $CeNi_2Sn_2$.

II. EXPERIMENTAL METHODS

Polycrystalline samples of $CeNi_2Sn_2$ and $LaNi_2Sn_2$ were prepared by arc-melting the pure elements in their stoichiometric ratio in an atmosphere of purified argon gas. The button was flipped several times and remelted to achieve good homogeneity. The samples were annealed at 800 K for 7 days. The overall weight loss during melting was less than 1%. X-ray measurements of the sample were carried out at room temperature and showed only a single phase in these series of samples. The x-ray powder diffractometer uses Cu $K\alpha_1$ radiation with a wavelength = 1.54056 Å. Table I is the index table of the x-ray-diffraction patterns for $CeNi_2Sn_2$. The structure is consistent with the tetragonal $CaBe_2Ge_2$ type (space group $P4/nmm$).[7] Figure 1 shows the x-ray-diffraction patterns of $CeNi_2Sn_2$ and $LaNi_2Sn_2$. The lattice parameters for $CeNi_2Sn_2$ are $a = 4.36(5)$ Å, $c = 10.21(2)$ Å and for $LaNi_2Sn_2$ are $a = 4.41(2)$ Å, $c = 10.17(2)$ Å, which are consistent with the report of Kaczmarska *et al.*[7] Table I is the index table of the x-ray-diffraction patterns for $CeNi_2Sn_2$, the $\chi^2 = (\theta_{observed} - \theta_{calculated})^2/N$ of this fitting is $(0.0567°)^2$, where N is the number of lines.

For $CeNi_2Sn_2$ and $LaNi_2Sn_2$, Ślebarski, Pierre, and Kaczmarska[8] reported that annealing in some cases is able to cause monoclinic distortion, observed by a small Bragg-line splitting. A similar behavior was also reported by Sampathkumaran *et al.*[9] However, as shown in Fig. 1, there is no x-ray line splitting for the x-ray-diffraction patterns of $CeNi_2Sn_2$ and $LaNi_2Sn_2$. It might be that our diffractometer

TABLE I. The index table of the x-ray-diffraction patterns for $CeNi_2Sn_2$.

$2\theta_{observed}$ (deg)	$d_{observed}$ (Å) $=\lambda/(2\sin\theta_{observed})$	$2\theta_{calculated}$ (deg)	$d_{calculated}$ (Å) $=\lambda/(2\sin\theta_{observed})$	$\Delta(2\theta)$ (10^{-2} deg)	*hkl*
26.3	3.386	26.27	3.390	3.29	003
28.7	3.108	28.74	3.103	4.20	110
29.95	2.981	30.02	2.974	7.00	111
33.4	2.681	33.42	2.678	2.50	103
35.3	2.541	35.27	2.542	2.90	004
41.15	2.192	41.28	2.185	13.4	200
46.15	1.965	46.20	1.963	4.00	114
49.85	1.828	49.95	1.824	10.00	212
53.85	1.701	53.91	1.699	6.20	213
59.75	1.546	59.81	1.545	5.80	220
62.35	1.488	62.44	1.486	8.95	116
66.45	1.406	66.44	1.406	1.00	223
69.85	1.345	70.01	1.338	16.00	303
74.5	1.273	74.59	1.271	9.00	008

(Rigaku, D/MAX-2500) is not sensitive enough to indicate the small line splitting of monoclinic distortion.

The L_{III} x-ray-absorption-spectroscopy (XAS) spectra of $CeNi_2Sn_2$ at 300 and 15 K were measured at SRRC (Synchrotron Radiation Research Center, Hsinchu, Taiwan, ROC) on the Wiggler x-ray beam line BL17C for Ce L_{III}-edge measurements. The samples used for XAS measurements were prepared by dusting the well-powdered samples onto the Scotch tape. The size of the powdered particles was made smaller than 37 μm by using a 400-mesh sieve to avoid the thickness effect.[10]

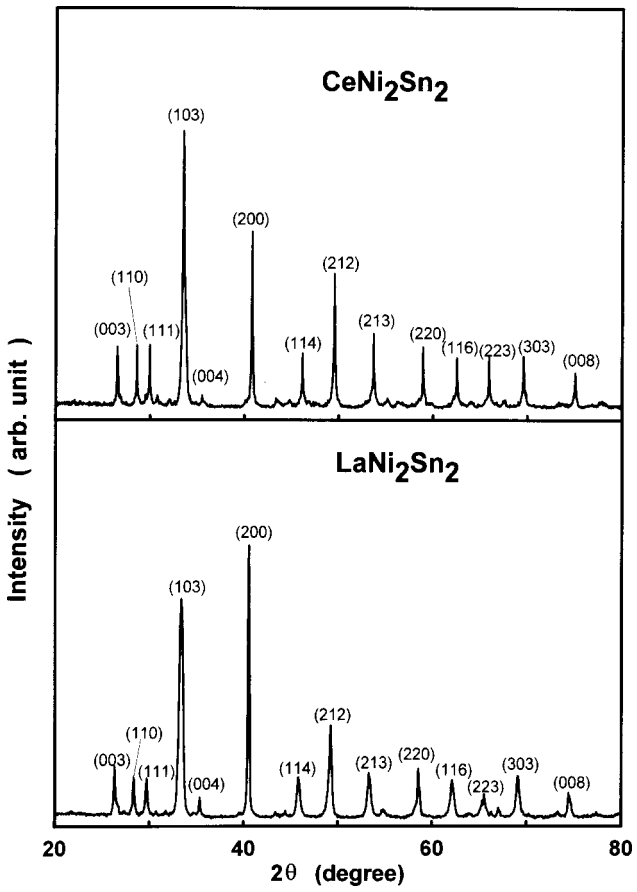

FIG. 1. The x-ray-diffraction patterns of $CeNi_2Sn_2$ and $LaNi_2Sn_2$.

The dc-magnetization studies were performed in a Quantum Design superconducting quantum-interference device (SQUID) magnetometer. Both the zero-field-cooling (ZFC) and the field-cooling (FC) methods measured the susceptibility. For ZFC, we cooled the sample from 300 to 2 K in the zero field and applied the field at 2 K. (By the low-field profiling option of the Quantum Design SQUID, we can measure a remnant field in the sample position. Without any applied field, the magnetic field in the sample position is $<0.000\,04$ T.) Then we heated the sample while measuring the χ in the constant field. For FC, the sample was cooled in a magnetic field from 300 to 2 K and then it was heated up while measuring the χ.

The ac magnetic properties of $CeNi_2Sn_2$ were measured by a Quantum Design physical property measurement system (PPMS). The electrical resistance was measured by a four-probe method. The resistance of a sample was measured by averaging the voltages obtained with the current in the forward and the reverse directions.

The specific-heat measurements $C(T)$ were performed in a Quantum Design PPMS. The γ of $CeNi_2Sn_2$ is $\sim$0.6 J/mol K^2, which agrees with the report of Takabatake *et al.*[5]

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the zero-field-cooled molar susceptibility $\chi_{ZFC}(T)$ and field-cooled molar susceptibility $\chi_{FC}(T)$ for $CeNi_2Sn_2$ in a 0.01-T magnetic field. The inset of Fig. 2 is the temperature dependence $1/\chi_{ZFC}(T)$ for $CeNi_2Sn_2$ in a 0.01-T magnetic field. The susceptibility follows approximately a Curie-Weiss law above 20 K with a negative Curie-Weiss temperature $\theta=-7.6$ K. The effective moment μ_{eff} deduced from the paramagnetic region is $2.67\mu_B$, which is slightly larger than the theoretical

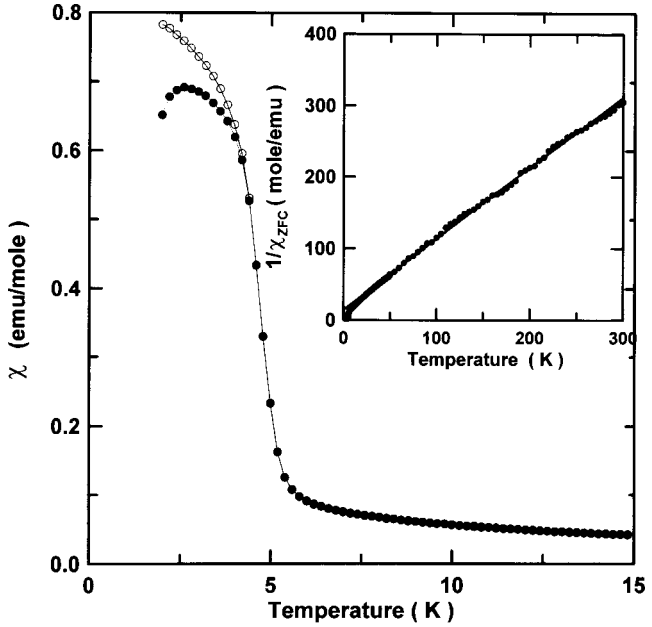

FIG. 2. The temperature dependence of the zero-field-cooled molar susceptibility $\chi_{\mathrm{ZFC}}(T)$ (●) and field-cooled molar susceptibility $\chi_{\mathrm{FC}}(T)$ (○) for $CeNi_2Sn_2$ at a 0.01 T magnetic field. The inset is the temperature dependence $1/\chi_{\mathrm{ZFC}}(T)$ for $CeNi_2Sn_2$ at a 0.01-T magnetic field.

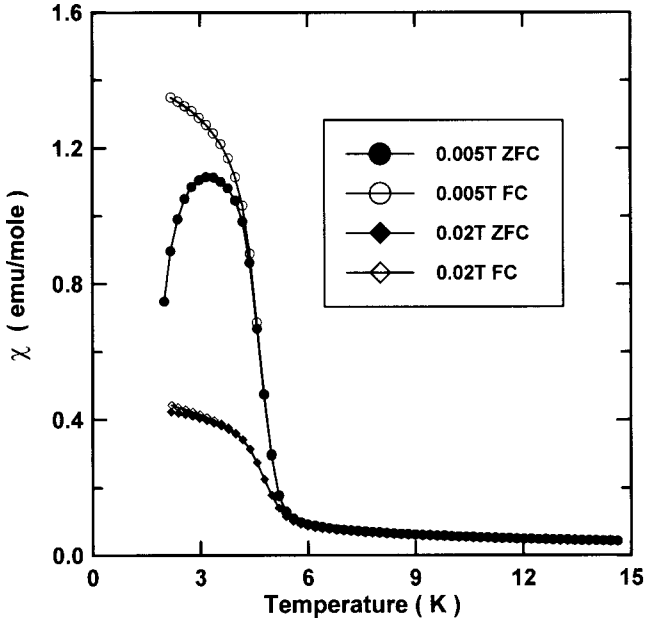

FIG. 3. The temperature dependence of the zero-field-cooled molar susceptibility $\chi_{\mathrm{ZFC}}(T)$ and field-cooled molar susceptibility $\chi_{\mathrm{FC}}(T)$ for $CeNi_2Sn_2$ at 0.005 and 0.02 T.

value of the Ce^{3+} free atom at the $^2F_{5/2}$ state $(2.54\mu_B)$.

The Curie-Weiss temperature of a polycrystalline $CeNi_2Sn_2$ significantly depends on an annealing procedure.[7] The Curie-Weiss temperature for our sample is closer to the data found earlier by Sampathkumaran *et al.*[9] (∼−5 K) and Kaczmarska *et al.*[7] (∼−19 K) than those found by Liang, *et al.* (∼−46 K) Jisrawi, and Crott[3] and Beyermann *et al.*[4] (−58 K). Kaczmarska *et al.*[7] claimed that the differences between Curie-Weiss temperatures of given works might arise mainly from a spurious phase, not detected by x-ray analysis and an unknown Pauli paramagnetic contribution. Therefore, the large effective moment μ_{eff} $(2.67>2.54\mu_B)$ and large negative Curie-Weiss temperature $(\theta=-7.6\ \mathrm{K})$ imply the existence of random magnetic moments from ''a spurious phase or unknown Pauli paramagnetic contribution'' in $CeNi_2Sn_2$.

A spin glass is a random, mixed-interacting, magnetic system characterized by random, yet cooperative, freezing of spins at a well-defined temperature T_f below which a highly irreversible, metastable frozen state occurs without the ordinary long-range spatial magnetic order.[11] In a spin glass, the ferromagnetic clusters are highly anisotropic and the magnetic relaxation time becomes so long as to give rise to the pronounced deviation of $\chi_{\mathrm{FC}}(T)$ from $\chi_{\mathrm{ZFC}}(T)$ below a characteristic temperature T_f.

As shown in Fig. 2, $\chi_{\mathrm{ZFC}}(T)$ starts to deviate from $\chi_{\mathrm{FC}}(T)$ at 5 K and displays a peak at 2.5 K, which indicates that the paramagnetic random magnetic moments correlate to form magnetic clusters below 5 K, and those magnetic clusters are further frozen to a spin-glass phase below the spin-freezing temperature $T_f=2.5$ K. Figure 3 shows $\chi_{\mathrm{ZFC}}(T)$ and $\chi_{\mathrm{FC}}(T)$ for $CeNi_2Sn_2$ at 50 and 200 Oe. Below 5 K, both $\chi_{\mathrm{ZFC}}(T)$ and $\chi_{\mathrm{FC}}(T)$ are depressed drastically by the magnetic field, which implies that the mechanism associated with random magnetic moments, forming magnetic clusters, is strongly affected by the field. The magnetic field smears out the peak of $\chi_{\mathrm{ZFC}}(T)$. Besides, as the magnetic field increases, the freezing temperature T_f decreases. Therefore, the field also considerably influences the mechanism that cooperates with magnetic clusters to form spin-glass phase.

For canonical spin glasses, in a spin-glass state or a magnetic cluster-frozen phase, it takes several decades to turn the magnetic moments toward the field direction. Figure 4 is the time dependence of zero-field-cooled magnetization $M_{\mathrm{ZFC}}(t)$ for $CeNi_2Sn_2$ at 2 K in a 0.005-T field. The solid line in Fig. 4 is the fitting curve of the stretched exponential function:

$$M_{\mathrm{ZFC}}(t)=M_0-M'\exp\left[-\left(\frac{t}{\tau}\right)^{1-n}\right],$$

with $\tau=917$ sec. The fitting values are indicated in Table II. The extremely large time constant τ is consistent with the existence of a spin-glass phase in $CeNi_2Sn_2$.

The time dependence of $M(t)$ in a spin-glass state could cause magnetization hysteresis. To confirm further the existence of cooperation among magnetic clusters in $CeNi_2Sn_2$, we measured the field dependence of magnetization $M(H)$ at 2 K. As shown in the inset of Fig. 4, the $M(H)$ of $CeNi_2Sn_2$ exhibits clear magnetization hysteresis.

It is well known in the case of canonical spin glasses that to undergo from a paramagnetic to a spin-glass transition as a function of decreasing temperature, the real (in-phase) component of magnetic ac susceptibility, χ' exhibits a cusp at the spin-freezing temperature T_f. For example, with measured frequency 234 Hz and applied oscillating field

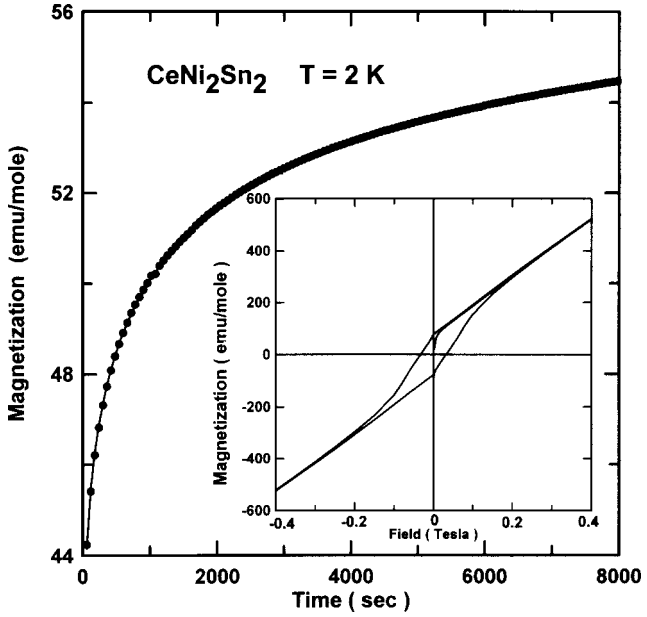

FIG. 4. The time dependence of zero-field cooled magnetization $M_{\mathrm{ZFC}}(t)$ for $CeNi_2Sn_2$ at 2 K in a 0.005-T field. The solid line is the fitting curve of stretched exponential function: $M_{\mathrm{ZFC}}(t)=M_0-M'\exp[-(t/\tau)^{1-n}]$ with $\tau=917$ s. The inset is the field dependence of magnetization $M(H)$ at 2 K.

$\leqslant$0.0001 T, the real part of the ac susceptibility (χ') of a canonical spin glass AuMn exhibits a sharp maximum at $T_f\sim 10.2$ K.[12]

Figure 5 indicates the temperature dependence of the real component of ac susceptibilities $\chi'(T)$ for $CeNi_2Sn_2$ in an ac field 0.0001 T at 200, 2000, 5000, 8000, and 10 000 Hz. For ac susceptibility measurements, we cooled the sample from 300 to 2 K without any applied field. Then we heated the sample while measuring the susceptibilities for 200, 2000, 5000, 8000, and 10 000 Hz simultaneously at each temperature. The most remarkable feature of $\chi'(T)$ is that there are two peaks at 4.6 and 5 K. Although the magnitude of peaks decreases as the frequency increases, the positions of these two peaks are independent of the frequency. Figure 6 is the temperature dependence of the imaginary component of ac susceptibilities $\chi''(T)$ for $CeNi_2Sn_2$ in an ac field 0.0001 T at 200, 2000, 5000, 8000, and 10 000 Hz. There are also two peaks at 4.4 and 5 K in $\chi''(T)$ for $CeNi_2Sn_2$. Since $CeNi_2Sn_2$ has antiferromagnetic order below $T_N=1.8$ K, which is much lower than 4 K, these two peaks can only be related to short-range magnetic order instead of a long-range order. There are two kinds of structures, tetragonal and

TABLE II. The fitting values of $M_{\mathrm{ZFC}}(t)=M_0-M'\exp[(-t/\tau)^{1-n}]$.

Field (T)	0.005
M_0 (emu/mole)	55.00 ± 0.083
M' (emu/mole)	20.49 ± 0.028
τ (s)	917 ± 14.4
n	0.69 ± 0.00046

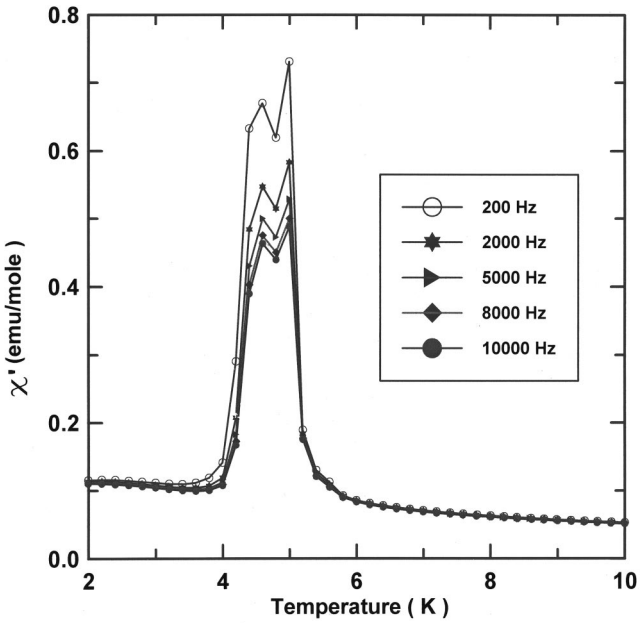

FIG. 5. The temperature dependence of the real component of ac susceptibilities $\chi'(T)$ for $CeNi_2Sn_2$ in an ac field of 0.0001 T at 200, 2000, 5000, 8000, and 10 000 Hz.

monoclinic ($\beta=90°48'$),[7] in $CeNi_2Sn_2$. If the lattice structure affects the cooperation of magnetic clusters, these two peaks might be related to two slightly different spin-freezing temperatures T_f of tetragonal and monoclinic structures in $CeNi_2Sn_2$.

To confirm further the magnetic behavior of $CeNi_2Sn_2$, Fig. 7 shows the temperature dependence of magnetization $M(T)$ without any applied field ($H<0.000\,04$ T). The inset

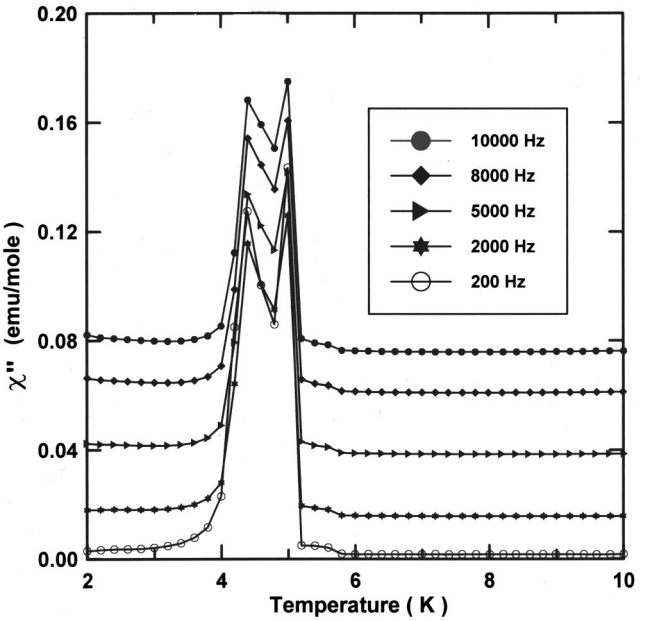

FIG. 6. The temperature dependence of the imaginary component of ac susceptibilities $\chi''(T)$ for $CeNi_2Sn_2$ in an ac field of 0.0001 T at 200, 2000, 5000, 8000, and 10 000 Hz.

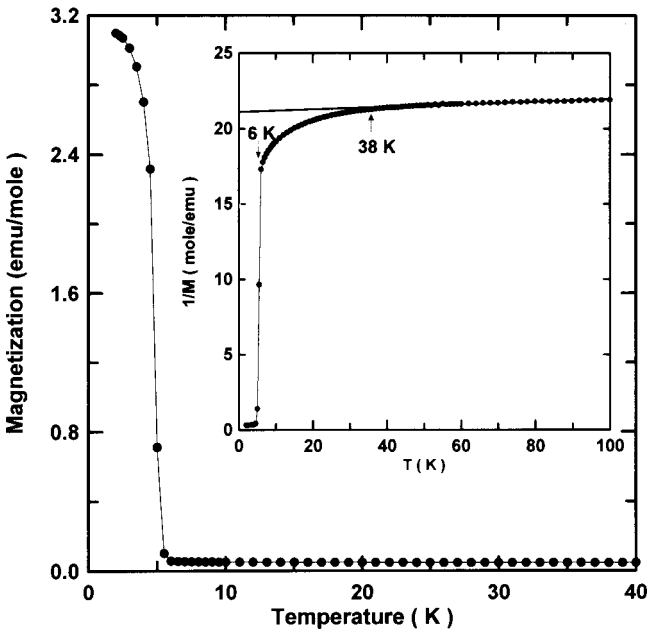

FIG. 7. The temperature dependence of magnetization $M(T)$ without any applied field. The inset is the inverse of magnetization $M^{-1}(T)$ versus temperature.

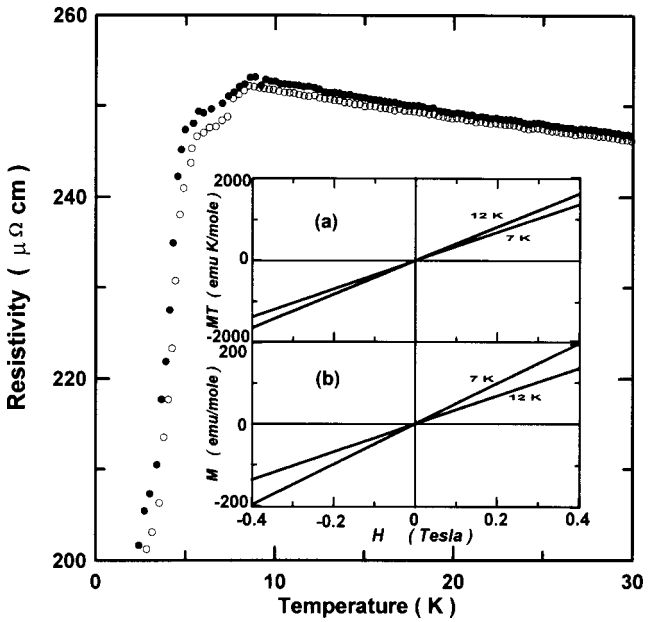

FIG. 8. The temperature dependence of zero-field-cooled electrical resistivity $\rho_{\mathrm{ZFC}}(T)$ (●) and field-cooled resistivity $\rho_{\mathrm{FC}}(T)$ (○) in a 0.0050-T magnetic field between 2 and 30 K.

of Fig. 7 is the inverse of magnetization $M^{-1}(T)$ versus the temperature. Above 38 K, the temperature dependence of $M^{-1}(T)$ can be described by $1/M(T)=cT+d$ with $c=0.008\,52$ mol emu^{-1} K^{-1} and $d=21.22$ mol emu^{-1}. It implies that paramagnetic random magnetic moments start to correlate below 38 K. Below ~6 K, the inverse of magnetization $M^{-1}(T)$ decreases rapidly as the temperature decreases and nears a constant at ~4 K, which might indicate that the magnetic clusters start to correlate at ~6 K, and freeze at ~4 K.

The temperature dependences of zero-field-cooled electrical resistivity $\rho_{\mathrm{ZFC}}(T)$ and field-cooled resistivity $\rho_{\mathrm{FC}}(T)$ of $CeNi_2Sn_2$ in a 0.005-T magnetic field between 2 and 30 K are shown in Fig. 8. First, we cooled the sample from 300 to 2 K without any applied field. Then we heated the sample up to 80 K while measuring the ρ_{ZFC} in the constant field. When the sample was cooled in a magnetic field from 80 to 2 K, we measured the $\rho_{\mathrm{FC}}(T)$. Above 10 K, the long tail of the Kondo effect, which has a negative temperature coefficient $(d\rho/dT<0)$, further confirms the existence of paramagnetic random magnetic moments in $CeNi_2Sn_2$. If the magnetic cluster is frozen in a spin-glass system, it takes a long time to turn the magnetic moments toward the field direction. However, the ordering of magnetic clusters will considerably reduce the resistivity. Therefore, as soon as magnetic clusters are formed, the zero-field-cooled resistivity $\rho_{\mathrm{ZFC}}(T)$ is different from the field-cooled resistivity $\rho_{\mathrm{FC}}(T)$, and both $\rho_{\mathrm{ZFC}}(T)$ and $\rho_{\mathrm{FC}}(T)$ will significantly decrease below the spin-freezing temperature T_f. In 0.005 T, $\rho_{\mathrm{ZFC}}(T)$ starts to deviate from $\rho_{\mathrm{FC}}(T)$ at ~8 K, which might indicate that paramagnetic random magnetic moments begin to develop magnetic clusters. The inset (a) of Fig. 8 is the magnetization M versus magnetic field H, and the inset (b) is the field dependence of $MT(H)$ at 7 and 12 K for $CeNi_2Sn_2$. The linear dependence of M on H indicates a paramagnetic order above 7 K. If the random paramagnetic moments do not correlate between 7 and 12 K, $MT(H)$ should be nearly temperature independent. As shown in inset (b), the $MT(H)$ at 7 K is meaningfully less than the $MT(H)$ at 12 K, which might further support that random paramagnetic moments begin to develop magnetic clusters below 8 K. Since there is no hysteresis in $M(H)$ at 7 K, at this temperature the correlation among clusters is not strong enough to form a spin-glass state.

At ~5 K, both $\rho_{\mathrm{ZFC}}(T)$ and $\rho_{\mathrm{FC}}(T)$ rapidly decrease as temperature decreases, which suggests that magnetic clusters might freeze below 5 K. As shown in the inset of Fig. 4, the hysteresis of $M(H)$ at 2 K additionally supports that the magnetic clusters further correlate below 5 K.

The specific heat C of polycrystal samples of $CeNi_2Sn_2$ and its isostructural nonmagnetic compound $LaNi_2Sn_2$ were reported by Takabatake *et al.*,[5] who found that there are two peaks in the magnetic specific heat at 1.8 and 7.2 K. [The magnetic specific heat C_m was defined as $C_m=C(CeNi_2Sn_2)-C(LaNi_2Sn_2)$]. They claimed that the 1.8-K peak was due to an antiferromagnetic order and the 7.2-K peak was induced by the crystal-field effect. However, Takabatake *et al.* also pointed out that the 7.2-K peak was much broader than expected for a simple Schottky contribution. In their measurements, the linear extrapolation of C/T from above 4 to 0 K yielded a large value of 0.65 J/K^2 mol.

Figure 9 shows the temperature dependence of specific heat $C(T)$ for $CeNi_2Sn_2$ and $LaNi_2Sn_2$. There is a broad peak in the magnetic specific heat $C_m(T)$ at 6 K. The inset of Fig. 9 is C/T versus T^2 between 2 and 5 K, the linear extrapolation of C/T from above 5 to 0 K yields a large value of 0.67 J/K^2 mol, which is consistent with the result of Takabatake *et al.*

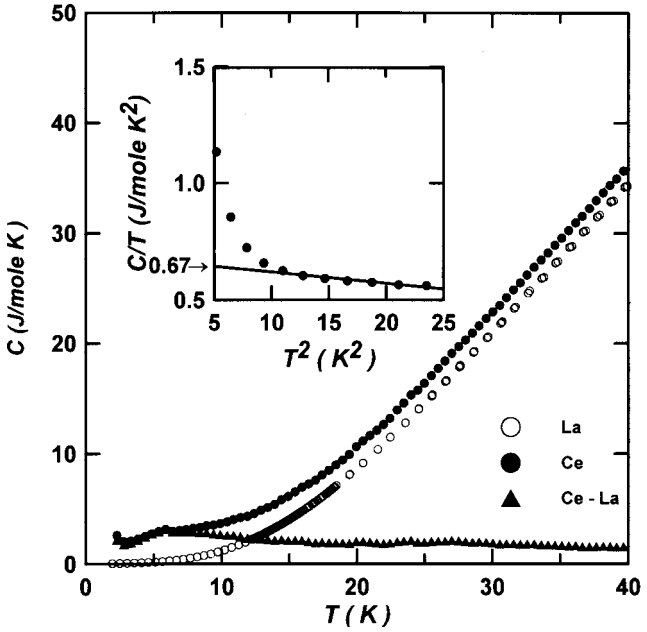

FIG. 9. The temperature dependence of specific heat $C(T)$ for $CeNi_2Sn_2$ (●) and $LaNi_2Sn_2$ (○). The magnetic specific heat C_m (▲) was defined as $C_m = C(CeNi_2Sn_2) - C(LaNi_2Sn_2)$. The inset is C/T versus T^2 between 2 and 5 K.

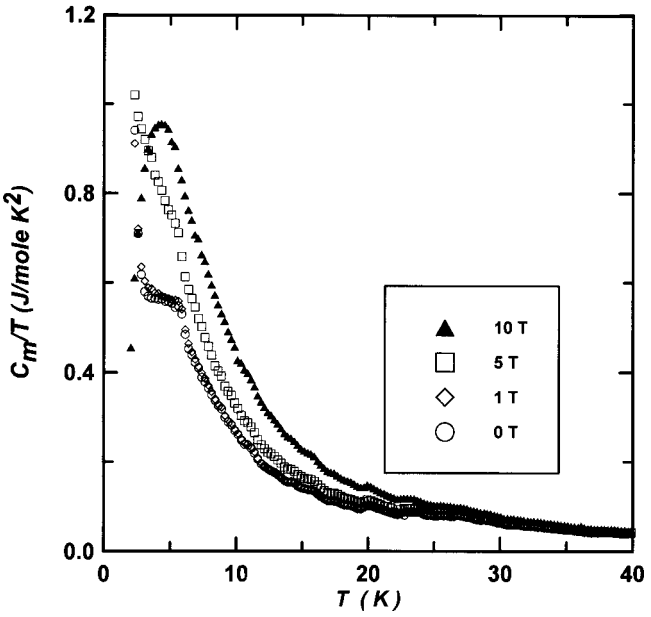

FIG. 10. The magnetic molar specific heat divided by temperature C_m/T versus temperature in 0, 1, 5, and 10 T for $CeNi_2Sn_2$. The magnetic specific-heat C_m is defined as $C_m = C(CeNi_2Sn_2) - C(LaNi_2Sn_2)$.

As pointed out by Takabatake *et al.*, the simplest interpretation of the 6-K peak of $C_m(T)$ for $CeNi_2Sn_2$ is due to low-lying crystal levels, since the $J=\frac{5}{2}$ multiplet of Ce^{3+} in the lattice symmetry lower than the cubic symmetry splits into three doublets. Using a CF-only model for $J=\frac{5}{2}$ Ce in the tetragonal symmetry, Takabatake *et al.* obtained three doublets 0, 17.2, and 218 K.[5] Because the splitting Δ between the ground state and the first excited CF doublet is much smaller than those of higher excited states, the specific heat due to the Schottky contribution is[13]

$$C_m(T) = R\frac{(\Delta/T)^2 e^{\Delta/T}}{(1+e^{\Delta/T})^2},$$

where R is the gas constant. Therefore, $C_m(T)$ has a maximum equal to $0.44R$ at $T_{max}=0.416\Delta$. If T_{max} is ~6 K, Δ is ~14.4 K. At 6 K, the magnetic specific heat $C_m(T)$ of $CeNi_2Sn_2$ is ~3.2 J/mol K, which equals $0.38R$. This value is slightly less than $0.44R$. [For the measurements of Takabatake *et al.*, T_{max} is ~7.2 K, and $C_m(7.2\text{ K}) \sim 2.8$ J/mol K, which is even less than 3.2 J/mol K.]

For the canonical spin glass 2790-ppm CuMn, [14] $C(T)$ exhibits a peak at $T'_{max} \sim 5$ K. The spin freezing temperature T_f of 2790-ppm CuMn is 3 K so that $T'_{max}=1.6T_f$. Since the spin freezing temperature of $CeNi_2Sn_2$ nears 3 K, the spin-glass phase will cause a maximum of $C(T)$ at ~5 K. Therefore, the peak of specific heat by a spin-glass phase (at 5 K) nears the peak of the Schottky anomaly (at 6 K). These two peaks will smear out each other, so that the maximum of $C_m(T)$ for $CeNi_2Sn_2$ is much broader than expected for a simple Schottky contribution. Namely, the depression of the Schottky peak might be attributed to the broadening of the Schottky anomaly by the magnetic clusters.

For a canonical spin glass, it shows that entropy shifts from the low-temperature to the high-temperature portion because a great deal of the magnetic entropy is lost or frozen out far above T_f.[14] And the applied field shifts even more entropy from the low-temperature to the high-temperature portion.[15] To confirm further the spin-glass order in $CeNi_2Sn_2$, we measured the magnetic entropy of $CeNi_2Sn_2$ in various magnetic fields. Figure 10 shows the molar specific heat divided by temperature C_m/T versus temperature for 0, 1, 5, and 10 T for $CeNi_2Sn_2$. As shown in Fig. 10, entropy shifts from the low temperature to high temperature. The shoulder of C_m/T, which corresponds to the maximum of C_m (at ~6 K), becomes less pronounced and disappears as $H>5$ T. Above 40 K, $C_m(T)$ is independent of the magnetic field. The magnetic entropy S_m is defined as

$$S_m = \int_{2\text{ K}}^{40\text{ K}} \frac{C_m}{T} dT.$$

As shown in Table III, S_m increases as the magnetic field increases. The field dependence of S_m further supports the existence of a spin-glass phase in $CeNi_2Sn_2$.

Between 40 and 30 K, $C_m(T)$ of $CeNi_2Sn_2$ can be described by $C_m(T)=\gamma T+\beta T^3$. Without any applied field, $\gamma = 112$ mJ mol^{-1} K^{-2} and $\beta = -0.0051$ mJ mol^{-1} K^{-4}. This γ value is much larger than those of normal metals. Since the γ is estimated within a high-temperature range ($40<T<30$ K), one should guard against associating the calculated γ with the ground-state enhancement of effect mass.

Spin-glass magnetism could induce a possible enlargement of specific heat.[16] As an example, the γ value of $CePd_3B_{0.3}$ is 150 mJ mol^{-1} K^{-2}.[17] Gschneidner *et al.*[18] suggested that the enhancement of γ is caused by a spin-glass

TABLE III. The fitting values γ and β of $C_m/T=\gamma+\beta T^2$, and magnetic entropy S_m for various magnetic fields. Between 40 and 30 K, the fitting values are defined as $\gamma=\gamma_1$ and $\beta=\beta_1$, and between 40 and 50 K, are defined as $\gamma=\gamma_2$ and $\beta=\beta_2$.

Field (T)	γ_1 (mJ mol^{-1} K^{-2})	β_1 (mJ mol^{-1} K^{-4})	γ_2 (mJ mol^{-1} K^{-2})	γ_2 (mJ mol^{-1} K^{-4})	S_m (J K^{-1} mol^{-1})
0	112	−0.0051	7.6	0.0175	6.426
1	110	−0.0050	6.1	0.0183	6.434
5	122	−0.0057	10	0.0168	8.24
10	146	−0.0071	18	0.0145	9.81

state that is due to the presence of atomic site disorder. In $CePd_3B_{0.3}$ the B atoms randomly occupy the body-center site of this antiperovskite crystal, which introduces a varying electronic environment around Ce ions and thus causes a variation in the Ruderman-Kittel-Kasuya-Yosida (RKKY) mediated-exchange interaction among the Ce ions. The interaction depends upon the boron occupation in the vicinity of Ce ions. It is this random Ce-Ce exchange interaction that gives rise to the spin-glass behavior; this accounts for the large observed γ value. Gschneidner *et al.* called this kind of material nonmagnetic atom-disorder spin glass (NMAD spin glass). With a large γ value, $CeNi_2Sn_2$ is not necessarily a heavy fermion.

Gschneidner *et al.* pointed out that the possible mechanisms that will enhance the γ value are (1) low-lying crystal levels, (2) a spin-glass phase, and (3) magnetic order at low temperature. Therefore, only if the estimated γ value is not affected by these three mechanisms can it be used to decide whether this compound is a heavy fermion. Figure 11 shows C_m/T versus T^2 in 0, 1, 5, and 10 T for $CeNi_2Sn_2$. Above 40 K, C_m/T is independent of the magnetic field. Within a small temperature range, C_m/T versus T^2 can be described by a line, $C_m/T=\gamma+\beta T^2$. The slope of C_m/T versus T^2 changes the sign at ~40 K. Therefore, the γ values determined from the temperature ranges above 40 K will be significantly smaller than those below 40 K. Between 40 and 30 K, the fitting values of $C_m/T=\gamma+\beta T^2$ are defined as $\gamma=\gamma_1$ and $\beta=\beta_1$, and between 40 and 50 K are defined as $\gamma=\gamma_2$ and $\beta=\beta_2$. As shown in Table III, β_1 is negative but β_2 is positive. The γ_1 is almost 10 times larger than γ_2, which indicates that below 40 K the Kondo effect is considerably enhanced so that the effective mass of conduction electrons significantly increases. The inset of Fig. 11 is the temperature dependence of resistivity $\rho(T)$ for $CeNi_2Sn_2$ between 10 and 80 K. The resistivity $\rho(T)$ exhibits a minimum at ~40 K, which further supports this argument.

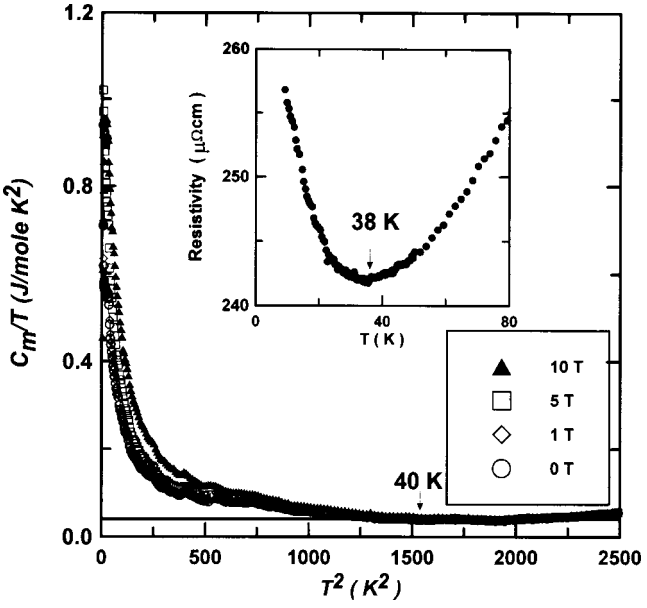

FIG. 11. C_m/T vs T^2 in 0, 1, 5, and 10 T for $CeNi_2Sn_2$. The inset is the temperature dependence of resistivity for $CeNi_2Sn_2$ between 10 and 80 K.

In a spin-glass phase, the magnetic field will significantly affect the specific-heat measurements. As shown in Table III, when the magnetic field is smaller than 5 T, γ_1 is almost a constant. Therefore, estimated values γ_1 between 40 and 30 K are not affected by the spin-glass phase in $CeNi_2Sn_2$. Furthermore, the temperatures of the antiferromagnetic ordering (~1.8 K) and Schottky peak (~7.2 K) for $CeNi_2Sn_2$ are so much lower than 30 K that magnetic order and crystal field do not affect γ_1 either. Hence, the large γ_1 ~112 mJ mol^{-1} K^{-2} strongly suggests that $CeNi_2Sn_2$ is not only a spin glass but also a true heavy fermion. If this argument is correct, $CeNi_2Sn_2$ might be a ''true'' heavy fermion with spin-glass behaviors.

As shown in Fig. 10, when the magnetic field is less than 5 T, below 3 K, C_m/T increases rapidly, which is due to the antiferromagnetic order at 1.8 K. However, at 10 T, below 3 K, C_m/T decreases rapidly and exhibits a peak at ~5 K. The easiest interpretation for this behavior is that in a high magnetic field (such as 10 T) one magnetic cluster will correlate with another to form a long-range magnetic order instead of a short-range spin-glass phase. Namely, in a high magnetic field (such as 10 T), there is a field-induced ferromagnetic-phase transition at ~5 K for $CeNi_2Sn_2$. Further experimental studies, for example, the low-temperature ($T<2$ K) and high-magnetic-field ($H>10$ T) specific-heat measurements are necessary to clarify this argument.

The heavy fermion can be considered as the $4f$ electron, hybridized with the conduction-band states near the Fermi surface via Kondo spin fluctuation. This process causes a strong mixing of the free conduction electrons with the localized $4f$ electrons and thus leads to an enormous enhancement of the linear specific-heat coefficient γ Brandt and

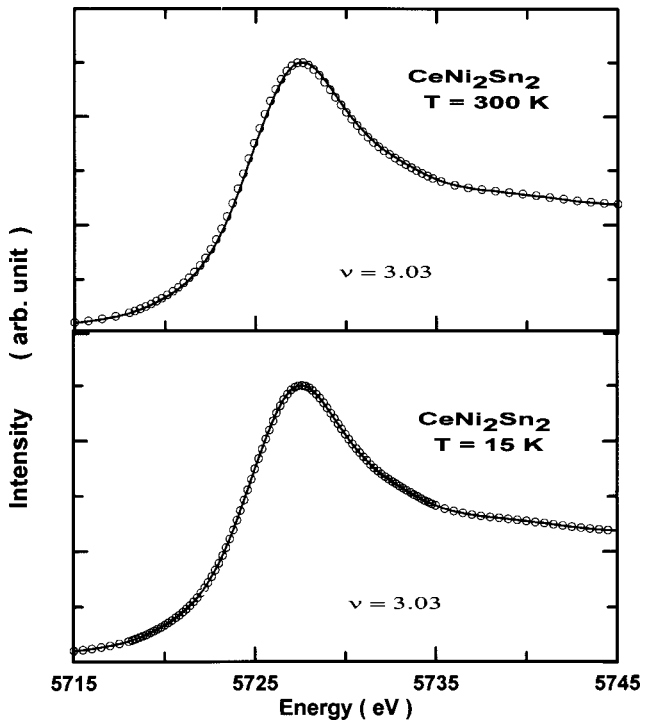

FIG. 12. The Ce L_{III}-edge spectra of $CeNi_2Sn_2$ at 300 and 15 K. The solid lines are fitting curves.

Moschalkov[19] and Rice and co-workers[20–24] implemented $\gamma \sim 1/(1-n_f)$, where the n_f is the occupation number of the $4f$ level. Therefore, for a heavy fermion $n_f \approx 1$. The valence ν of a Ce ion in $CeNi_2Sn_2$ is $\nu = 4 - n_f$. Hence, if the valence ν of Ce ions is very close to 3, it would further support $CeNi_2Sn_2$ to be a heavy fermion.

The L_{III} x-ray absorption spectroscopy is a very useful tool to measure the valence in mixed-valence systems. Figure 12 is the Ce L_{III}-edge spectra of $CeNi_2Sn_2$ at 300 and 15 K. To compare the intensity in the Ce-peak region, these two spectra are normalized to the Ce^{3+} peak. By fitting L_{III} spectra with a superposition of Ce^{3+} and Ce^{4+} edges, one obtains the Ce valence of $CeNi_2Sn_2$. The solid lines in Fig. 12 are fitting curves with $\nu = 3.03 \pm 0.015$. The details of the fitting procedure have been discussed in the reports of Liang[25] and Croft *et al.*[26]

The XAS measurement of $CeNi_2Sn_2$ was first reported by Liang, Jisravi, and Croft.[27] In their measurement, Ce in $CeNi_2Sn_2$ is trivalent or nearly trivalent. Usually, the error limit is around 5% in XAS measurements for estimating the valence. Therefore, our result is still consistent with that of Liang, Jisravi, and Croft.

The $3d$ core-level x-ray photoemission spectroscopy (XPS) measurements of $CeNi_2Sn_2$ were reported by Ślebarski *et al.*[28] In the $3d$ core-hole XPS spectrum of $CeNi_2Sn_2$, there is a shake-up-type satellite. This satellite can be interpreted as a contribution of the $4f$ configuration to the Ce ground state (it means that Ce shows a fractional intermediate valence larger than 3) or plasmon effect. Since this high-energy satellite is broad, Ślebarski *et al.* claimed that the satellite of the XPS spectrum is due to the plasmon excitation and the Ce ions of $CeNi_2Sn_2$ are in the form of a stable configuration. The message that valence of Ce in $CeNi_2Sn_2$ is very close to 3 further supports that $CeNi_2Sn_2$ is a heavy fermion.

IV. SUMMARY AND CONCLUSION

In $CeNi_2Sn_2$, the following observations were noted: (1) $\chi_{\mathrm{FC}}(T)$ significantly deviates from $\chi_{\mathrm{ZFC}}(T)$ below 3 K, (2) there are two peaks at ~4 and ~5 K in both the real (χ') and imaginary (χ'') components of ac susceptibilities, (3) the zero-field-cooled magnetization $M_{\mathrm{ZFC}}(t)$ is frozen at 2 K in a 0.005-T field with an enormous time constant 917 sec, (4) the temperature dependence of magnetization $M(T)$ without any applied field increases rapidly as the temperature is below ~6 K and nears a constant at ~4 K, (5) the $M(H)$ of $CeNi_2Sn_2$ exhibits clear magnetization hysteresis at 2 K, (6) at 0.005 T, $\rho_{\mathrm{ZFC}}(T)$ starts to deviate from $\rho_{\mathrm{FC}}(T)$ at ~8 K, and both $\rho_{\mathrm{ZFC}}(T)$ and $\rho_{\mathrm{FC}}(T)$ rapidly decease as the temperature decreases below 5 K, (7) the 6-K peak of $C_m(T)$ is much broader than expected for a simple Schottky contribution, and (8) the applied field shifts entropy from the low-temperature to the high-temperature portion. All these observations suggest a spin-glass phase below 3 K.

Actually, for a perfect single crystal, there is no random magnetic moment (magnetic cluster). Therefore, there is unlikely a spin-glass phase in a ''perfect'' single crystal. Spin-glass behaviors must relate to the impurity and the defect. In fact, many canonical spin-glass materials are composed of magnetic impurities. For examples, $Au_{95}Fe_5$ and $Cu_{95}Mn_5$, these spin-glass phases are due to magnetic impurities in nonmagnetic host metals. We do need ''magnetic impurity'' to form clusters that might correlate to form a spin-glass phase. Therefore, we need mechanisms which could create ''magnetic impurity'' or ''defect.'' In a spin glass, the possible mechanisms are (A) structure instabilities (random-site-type spin glass) and (B) magnetic instabilities (random-bond-type spin glass).

There exist two allotropic structures in $CeNi_2Sn_2$. The competition between different crystal structures will cause the structure instability. The structure instability might create the spin-glass-type short-range correlation among Ce ions. However, Pierre *et al.*[29] found that only a small displacement of Ce atoms is related to the monoclinic distortion, and that distortion is not expected to change the magnetic feature significantly. Besides, we have not observed the monoclinic phase in our x-ray-diffraction patterns of $CeNi_2Sn_2$. Therefore, even though some spin-glass-like behaviors might be related to the structure instability, the monoclinic distortion itself would not cause the spin-glass-like behaviors of $CeNi_2Sn_2$.

The magnetic structure of $CeNi_2Sn_2$ was reported by Pierre *et al.*[29] with refined magnetic-neutron-diffraction spectra. An important feature of the observed magnetic structure is frustration: Antiferromagnetism occurs in the basal (a,b) planes; thus the Ce atom at the center of the tetragonal cell ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) has vanishing spin-quadratic interaction with those of neighboring planes. One general effect of the frustration of magnetic interaction is the lowering of the long-range-ordering temperature and the occurrence of the short-

range order above this temperature.[30] Frustration is an important source of spin glasses.

For $CeNi_2Sn_2$, the linear specific-heat coefficient γ estimated from a temperature range (40–30 K) is $\sim$112 $mJ\,mole^{-1}\,K^{-2}$, which is not affected by low-lying crystal levels or spin-glass phase, or magnetic order at low temperature. This large γ value strongly suggests that $CeNi_2Sn_2$ is not only a spin glass but also a true heavy fermion.

By XAS measurement, the occupation number of the $4f$ level n_f of $CeNi_2Sn_2$ is $\sim$1. Therefore, for $CeNi_2Sn_2$, the $4f$ level of Ce is adequately close to but still almost entirely below the Fermi surface. The conduction electrons near Fermi level hybridize with the localized $4f$ electrons via Kondo spin fluctuation to form a heavy fermion. If the above opinions are correct, $CeNi_2Sn_2$ might be a ''true'' heavy fermion with spin-glass behaviors.

For $CeNi_2Sn_2$ in 10 T, the temperature dependence of C_m/T exhibits a peak at $\sim$5 K. The easiest interpretation for this behavior is that, in a high magnetic field, there is a field-induced ferromagnetic phase transition at $\sim$5 K. Further experiment, for example, the low-temperature ($T<2$ K) and high magnetic-field ($H>10$ T) specific-heat measurements are necessary to clarify this opinion.

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[1] R. V. Skolozdra, V. M. Mandzyk, Yu. K. Gorelenko, and V. D. Tkachuk, Fiz. Met. Metalloved. **52**, 966 (1981).
[2] M. Selsane, M. Lebail, N. Hamdaoui, J. P. Kappler, H. Noel, J. C. Achard, and C. Godart, Physica B **163**, 213 (1990).
[3] G. Liang, N. Jisrawi, and M. Croft, Physica B **163**, 134 (1990).
[4] W. P. Beyermann, M. F. Hundley, P. C. Canfield, J. D. Thompson, M. Latroche, C. Godart, M. Selsane, Z. Fisk, and J. L. Smith, Phys. Rev. B **43**, 13 130 (1991).
[5] T. Takabatake, F. Teshima, H. Fujii, S. Nishigori, T. Suzuki, T. Fujita, Y. Yamaguchi, and J. Sakurai, J. Magn. Magn. Mater. **90-1**, 474 (1990).
[6] Vladimir V. Gridin, Sergei A. Sergeenkov, André M. Strydom, and Paul de V. du Plessis, Phys. Rev. B **50**, 12 995 (1994).
[7] K. Kaczmarska, J. Pierre, A. Slebarski, and R. V. Skolozdra, J. Alloys Compd. **196**, 165 (1993).
[8] A. Ślebarski, J. Pierre, and K. Kaczmarska, J. Magn. Magn. Mater. **140-144**, 893 (1995).
[9] E. V. Sampathkumaran, S. K. Dhar, N. Nambudripad, and R. Vijayarahavan, Solid State Commun. **67**, 945 (1988).
[10] *Theoretical and Experimental Aspects of Valence Fluctuation and Heavy Fermions*, edited by L. C. Gupta and S. K. Malik (Plenum, New York, 1988).
[11] J. A. Mydosh, *Spin Glass: An Experimental Introduction* (Taylor & Francis, London, 1993).
[12] C. A. M. Mulder, A. J. van Duyneveldt, and J. A. Mydosh, Phys. Rev. B **25**, 515 (1982).
[13] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976).
[14] G. E. Brodale, R. A. Fisher, W. E. Fogle, N. E. Phillips, and J. van Curen, J. Magn. Magn. Mater. **31-34**, 1331 (1983).
[15] O. Meschede, F. Steglich, W. Felsch, H. Maletta, and W. Zinn, Phys. Rev. Lett. **44**, 102 (1980).
[16] S. K. Dhar, K. A. Gschneidner, Jr., C. D. Bredl, and F. Steglich, Phys. Rev. B **39**, 2439 (1989).
[17] O. Sologub, K. Hiebl, P. Rogl, and O. I. Bodak, J. Alloys Compd. **227**, 37 (1995).
[18] K. A. Gschneidner, Jr., J. Tang, S. K. Dhar, and A. Goldman, Physica B **163**, 507 (1990).
[19] N. B. Brandt and V. V. Moschalkov, Adv. Phys. **33**, 373 (1984).
[20] T. M. Rice and K. Ueda, Phys. Rev. Lett. **55**, 995 (1985).
[21] T. M. Rice and K. Ueda, Phys. Rev. B **34**, 6420 (1986).
[22] T. M. Rice, K. Ueda, H. R. Ott, and H. Rudigier, Phys. Rev. B **31**, 594 (1985).
[23] C. Gros, R. Joyut, and T. M. Rice, Phys. Rev. B **36**, 381 (1987).
[24] D. Baeriswyl, C. Gros, and T. M. Rice, Phys. Rev. B **35**, 8391 (1987).
[25] G. Liang, Ph.D. dissertation, Rutgers, The State University of New Jersey, 1990.
[26] M. Croft, R. Neifeld, C. U. Segre, S. Raaen, and R. D. Parks, Phys. Rev. B **30**, 4164 (1984).
[27] G. Liang, N. Jisravi, and M. Croft, Physica B **163**, 134 (1990).
[28] A. Ślebarski, A. Jezierski, A. Zygmunt, M. Neumann, S. Mähl, and G. Borstel, J. Magn. Magn. Mater. **159**, 179 (1996).
[29] J. Pierre, B. Lambert-Andron, R. V. Skolozdra, J. Rodriguez-Cavajal, and K. Kaczmarska, Physica B **202**, 143 (1994).
[30] P. Lacorre, J. Phys. C **20**, L775 (1987); P. Lacorre, Ph. D. dissertation, Université du Maine, Le Mans, France, 1988.