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Electric, magnetic, and thermal properties of Ce_2NiGe_3: A Kondo lattice compound showing spin glass behavior

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The magnetism of Ce_2NiGe_3 was investigated by measuring magnetic susceptibility χ, electrical resistivity ρ, thermoelectric power S, and specific heat C. dc susceptibility shows irreversible behavior at low temperatures. In a low external magnetic field, the field-cooled susceptibility increases monotonically with decreasing temperature. On the other hand, the zero-field-cooled susceptibility shows a peak at 3.5 K, which was estimated as the freezing temperature T_{f}. The magnitude of the peak decreases with increasing field. No anomalies were found in resistivity and in specific heat at T_{f}. Instead, a broad peak of the specific heat was observed at a higher temperature $1.3T_{\mathrm{f}}$. The magnetic contribution to the specific heat C_{m} shows a Schottky peak around 60 K, giving the scheme of crystal field splitting: $\Delta_1 = 135$ K and $\Delta_2 = 498$ K. The specific heat coefficient γ was estimated to be 25 mJ/K^2 mol Ce from the data below 1 K. Magnetic resistivity shows a $-\ln T$ dependence from room temperature to 50 K. The thermoelectric power shows a broad positive peak around 80 K and a negative peak at 20 K. Ce_2NiGe_3 was found to be a new Kondo lattice compound showing spin-glass behavior. Frustration and disorder play a crucial role in the formation of the spin-glass state.

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I. INTRODUCTION

Up to 20 ternary germanides can be synthesized in the Ce-Ni-Ge system.[1] Various ground states were realized due to the competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo interaction. For example, $CeNi_2Ge_2$ is a heavy-fermion compound showing deviations from Fermi-liquid behavior at low temperatures.[2] CeNiGe is an intermediate valence compound.[3] On the other hand, Chevalier *et al.* reported that the compounds containing 50 at. % of Ge or more, such as $Ce_2Ni_3Ge_5$, order antiferromagnetically at low temperatures.[4] Although Ce_2NiGe_3 was known to crystallize in AlB_2-type structure,[5] its magnetic properties were not studied yet to the best of our knowledge. It contains 50 at. % of Ge, locating at the boundary of the magnetic phase and nonmagnetic phase. The random distribution of T and X atoms in R_2TX_3 (R=U, Ce; T = transition metals; X=Ge, Si) usually gives rise to a random exchange interaction between R-R, which is one of the ingredients for spin-glass state to form. In fact, spin-glass behavior has been observed in U_2PdSi_3 (Refs. 6 and 7), U_2CoSi_3 (Ref. 8), and Ce_2AgSn_3 (Ref. 9). Thus, spin-glass behavior in Ce_2NiGe_3 is expected due to the random distribution of Ni and Ge atoms on the crystallographic sites. Spin-glass behavior is identified mostly in dilute metallic alloys.[10] Recently, observation of spin-glass behavior in ordered *f*-electron and *d*-electron systems has attracted much attention from both experimental and theoretical viewpoints.[11–13]

In this paper, we show the evidence for the formation of a spin-glass state in Ce_2NiGe_3 by studies of the magnetic, transport, and thermal properties. Plenty of experimental data have been accumulated for the thermoelectric power (TEP) of Ce compounds having antiferromagnetic, ferromagnetic, or nonmagnetic ground state. However, very few experimental reports on the TEP of the Ce compounds showing spin-glass behavior in the literature. We discussed the TEP result of Ce_2NiGe_3 on the basis of the theoretical work of Fischer.[14]

II. EXPERIMENT

Polycrystalline samples of Ce_2NiGe_3 and La_2NiGe_3 were prepared by arc melting the stoichiometric constitution elements in an argon atmosphere. Successively, the as-cast ingots were annealed for 1 week at 850 °C. dc magnetic susceptibility χ measurements down to 2 K were carried out by the use of a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design Co., Ltd.). Electrical resistivity ρ was measured using the conventional dc four-probe method. Thermoelectric power S was measured from 2 K to 300 K with a differential method by using the thermal couples of Chromel/Au+0.7 at. % Fe. Specific heat C was measured with a quasiadiabatic method in the temperature range 0.3–150 K.

III. EXPERIMENTAL RESULTS

X-ray diffraction confirmed that both Ce_2NiGe_3 and La_2NiGe_3 crystallize in AlB_2-type structure. The lattice parameters are $a = 4.164$ Å, $c = 4.243$ Å for the former and $a = 4.188$ Å, $c = 4.319$ Å for the latter. For both of them, only one weak peak near the (101) reflection could not be indexed. By comparing the simulated diffraction patterns of some phases close to Ce_2NiGe_3, the impurity is considered to be likely $CeNiGe_2$ although no trace of anomaly due to its antiferromagnetic ordering at 3.9 K was found in our measurement of susceptibility, resistivity and specific heat.

Figure 1(a) shows the magnetic susceptibility of Ce_2NiGe_3 measured under a low external magnetic field of 5

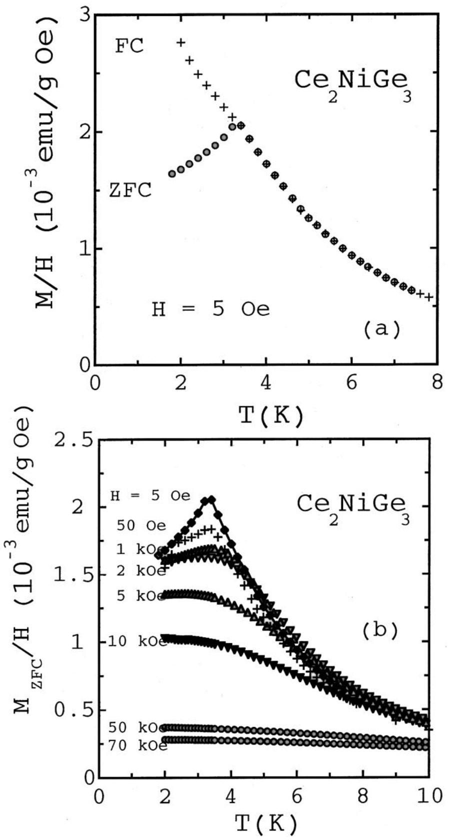

FIG. 1. (a) dc magnetic susceptibility M/H of Ce_2NiGe_3 measured after zero-field cooling (ZFC) and field cooling (FC) in a field of 5 Oe. (b) Temperature dependence of M_{ZFC}/H of Ce_2NiGe_3 measured in several external fields.

Oe. The sample was cooled down to 2 K from room temperature in zero field at first. Then, we set the magnetic field to 5 Oe and measured the zero-field-cooled (ZFC) susceptibility, $\chi_{ZFC}=M_{ZFC}/H$, while heating it to 10 K. χ_{ZFC} shows a distinct peak around 3.5 K. On the other hand, the field-cooled (FC) susceptibility, noted as $\chi_{FC}=M_{FC}/H$, was obtained by measuring the magnetization after cooling the sample from room temperature to 2 K in the field of 5 Oe. χ_{FC} monotonically increases with decreasing temperature. It can be seen that the susceptibility is irreversible below 3.5 K, which could be estimated as the freezing temperature T_f. The irreversibility of magnetic susceptibility below T_f is one of the characteristic behaviors of a spin-glass system.[15,16] The discrepancy between χ_{ZFC} and χ_{FC} could not be observed in a field stronger than 1 kOe. As can be seen in Fig. 1(b), the peak of χ_{ZFC} become broader while increasing the strength of field. A field stronger than 10 kOe suppressed the peak completely.

Figure 2 shows the susceptibility of Ce_2NiGe_3 in a field of 2 kOe. Above 70 K, χ follows a Curie-Weiss law, giving the effective moment $\mu_{eff}=2.45\mu_B$ and the paramagnetic Curie temperature $\theta_p=-4.6$ K. Here μ_{eff} is near to that of a free Ce^{3+} ion $(2.54\mu_B)$. In Ce_2NiGe_3, Ni ions do not carry magnetic moments. The inset shows $M(H)$ curves measured at various temperatures. Above 20 K, a linear relationship between M and H was observed. At low temperatures below

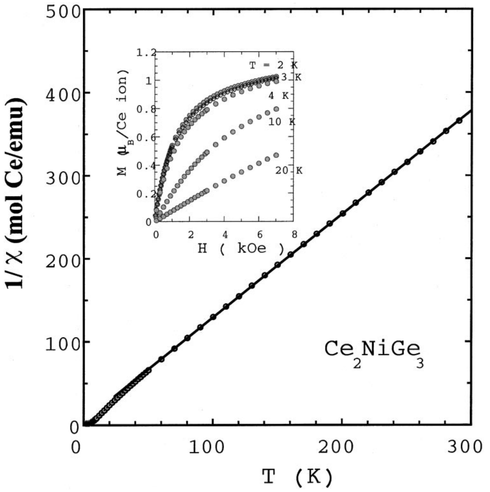

FIG. 2. Temperature dependence of $1/\chi$ of Ce_2NiGe_3 measured in an external field of 2 kOe. Inset shows the $M(H)$ curves measured in several temperatures.

10 K, the magnetization curves deviate from a linear relationship between M and H. At 2 K, a hysteresis loop with small remanet magnetization $(0.005\mu_B/Ce)$ was observed.

In a spin-glass state, the isothermal remanet magnetization (IRM) takes a long time to decay. The relaxation process of Ce_2NiGe_3 was investigated. At first, the sample was zero-field cooled to 2 K from room temperature. Then, a field was applied for 10 min and the IRM was measured as a function of time t after switching off the field $(t=0)$. The results for fields of $H_1=10$ kOe and $H_2=20$ kOe are displayed in Fig. 3. The solid lines in the figure are fitting results by using of a formula $M(t)=M(0)+\alpha \ln t$ with $M(0)=0.100$ (emu/g), $\alpha=-0.0043$ (emu/g) for H_1 and $M(0)=0.102$ (emu/g), $\alpha=-0.0048$ (emu/g) for H_2. The coefficient α is called *magnetic viscosity*. The experimental results can be reproduced excellently by using the formula as in the case of AuFe with 8% Fe, which is a typical spin glass.[17] The decay process of IRM is not universal for all spin glasses. For example, the

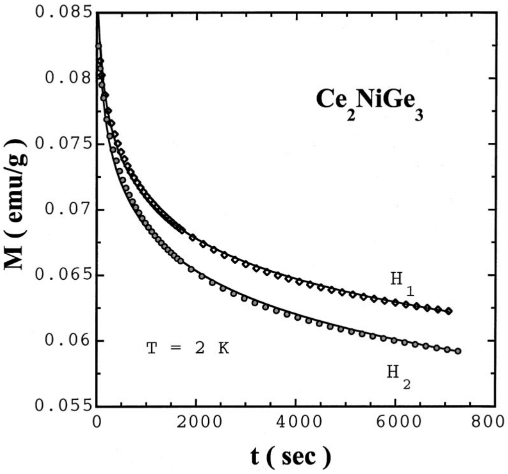

FIG. 3. Time dependence of isothermal remanent magnetization (IRM) of Ce_2NiGe_3 measured at 2 K. The solid lines are fitting results for $H_1=10$ kOe and $H_2=20$ kOe (see text).

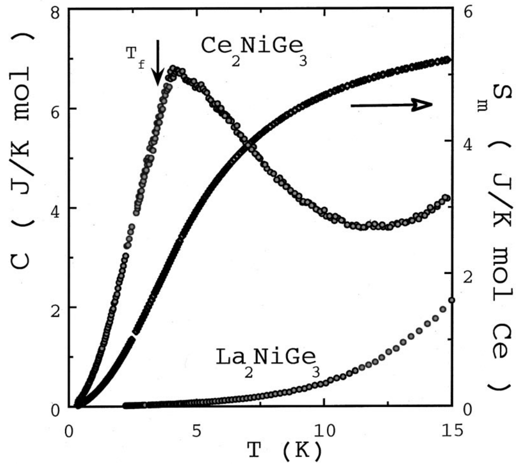

FIG. 4. Low-temperature specific heat of Ce_2NiGe_3 and La_2NiGe_3 together with the magnetic entropy S_m.

time dependence of IRM for U_2PdSi_3 (Ref. 7) was described by adding the third exponential term to the formula mentioned above. The difference could come from the details of the ingredients for the formation of a spin glass. However, it is common that IRM of a spin glass takes several decades to decay below its freezing temperature.[10]

The specific heat of La_2NiGe_3 and Ce_2NiGe_3 below 15 K is shown in Fig. 4. The specific heat of La_2NiGe_3 below 6 K can be described with a formula $C(T) = \gamma T + \beta T^3$ with $\gamma = 7.2$ mJ/K^2 mol and $\beta = 0.3345$ mJ/K^4 mol. This gives an estimation of the Debye temperature of 180 K. Here $C(T)$ of Ce_2NiGe_3 did not show any anomaly at T_f. Instead, a broad peak appears around a higher temperature $T = 4.5$ K$= 1.3$ T_f. Also, $C(T)$ shows a linear temperature dependence below T_f down to 1 K. The magnetic contribution to specific heat was obtained by defining $C_m(T) = C(T)_{Ce_2NiGe_3}$-$C(T)_{La_2NiGe_3}$. Magnetic entropy $S_m = \int_0^T C_m(T)/T dT$ was estimated and is shown in Fig. 4. Typically, about one-third of the total magnetic entropy is attained by the spin glass at $T = T_f$. For Ce_2NiGe_3, the magnetic entropy gain reaches 25% of R ln 2 at 3.5 K, which is comparable with the typical case.[15] $C_m(T)$ from 2 K to 150 K is shown in Fig. 5. A Schottky anomaly around 60 K was observed. In the hexagonal system, the ground state of Ce^{3+} was split into three doublets. Fitting the contribution from the crystal electric field (CEF) excitation to the specific heat gives the energy scheme $\Delta_1 = 135$ K and $\Delta_2 = 498$ K from the ground state, respectively. Neutron diffraction experiments are desired to check the CEF energy splitting scheme and the absence of long-range magnetic ordering.

The electrical resistivity of La_2NiGe_3 and Ce_2NiGe_3 is shown in Fig. 6 together with magnetic resistivity, $\rho_m = \rho_{Ce_2NiGe_3}$-$\rho_{La_2NiGe_3}$. No anomaly was observed at T_f. Here ρ_m shows a portion of the $-\ln T$ dependence from room temperature to 50 K and another portion of a very faint $-\ln$ T dependence from 20 K to 5 K, corresponding to the the Kondo effect with the presence of a hexagonal crystal field.

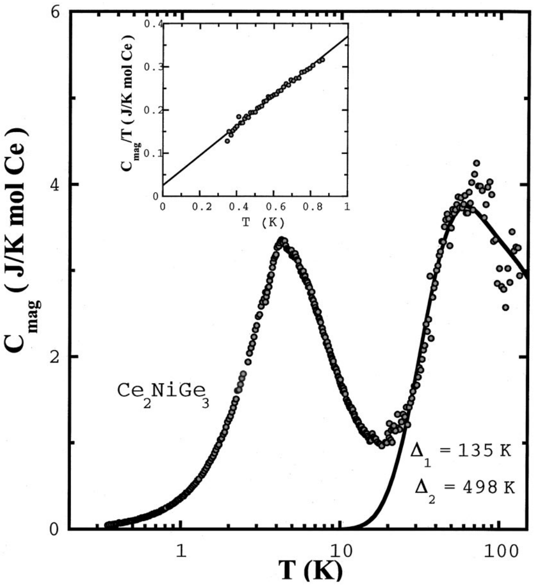

FIG. 5. Magnetic specific heat of Ce_2NiGe_3. The solid line is a Schottky fitting result (see text). Inset shows the C_m/T vs T below 1 K.

The thermoelectric power $S(T)$ of La_2NiGe_3 and Ce_2NiGe_3 is shown in Fig. 7. Here $S(T)$ of La_2NiGe_3 looks like normal metals, showing a small value and nearly a linear temperature dependence. On the other hand, $S(T)$ of Ce_2NiGe_3 shows a broad positive peak around 80 K and a negative peak at 20 K. The sign change occurred at a temperature of $T_0 \approx 10 T_f$. No anomaly was observed at T_f.

IV. DISCUSSION

Evidence for the spin-glass transition at 3.5 K in Ce_2NiGe_3 has been seen from the experimental results: (1) irreversible magnetic susceptibility and its response to the external field, (2) a long decay process of isothermal remanet magnetization, and (3) a broad peak of C at $T = 1.3 T_f$. Both the frustration and disorder, two ingredients resulting in a

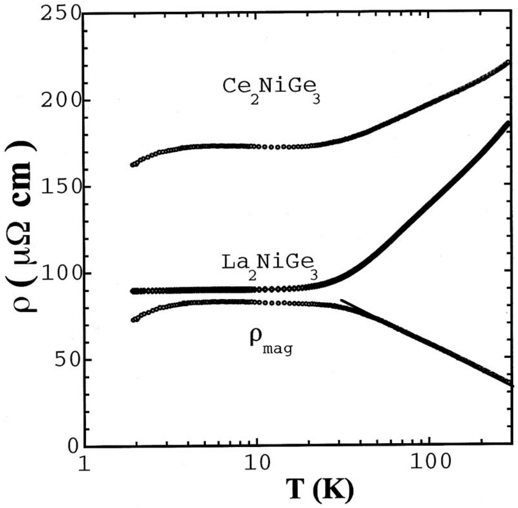

FIG. 6. Electrical resistivity of Ce_2NiGe_3 and La_2NiGe_3. $\rho_m = \rho_{Ce_2NiGe_3}$-$\rho_{La_2NiGe_3}$.

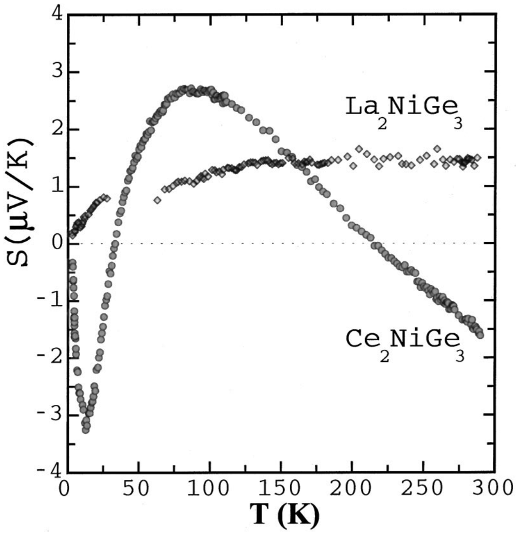

FIG. 7. Thermoelectric power of Ce_2NiGe_3 and La_2NiGe_3.

spin-glass state, are believed to play an essential role in Ce_2NiGe_3. Considering the hexagonal AlB_2-type crystal structure of Ce_2NiGe_3, the layers of Ce ions alternate with layers of Ni and Ge. The interlayer Ce ions on $1(a)$ sites form triangular network. Ni and Ge atoms distribute randomly on $2(c)$ sites. The large residual resistivity could be an indication of this randomness. The nearest-neighbor Ce-Ce exchange coupling J_1 occurs in the Ce layers and the next-nearest-neighbor Ce-Ce exchange coupling J_2 comes from the intralayer. $|J_1|$ and $|J_2|$ are possibly comparable because of the closeness of the lattice parameters a and c. Thus, a strong frustration will occur if J_1 and J_2 have opposite sign. Furthermore, the random distribution of Ni and Ge atoms may result in a random distribution of RKKY exchange coupling although Ce ions occupy only one kind of site. In U_2PdSi_3 (Ref. 7) and Ce_2AgIn_3 (Ref. 9), similar spin-glass behavior was also observed.

Special caution should be taken when one analyzes the low-temperature specific heat results of a spin glass. Gschneidner *et al.* pointed out that a large C/T value may mislead one to classify a spin glass into a heavy-fermion system.[18] A spin-glass transition or low-lying CEF levels can result in the large C/T. In order to clear this issue for the present system, measurement of specific heat was carried out down to 0.3 K, being much lower than T_{f}. Analysis of C_{m} gave CEF splitting of Ce_2NiGe_3: $\Delta_1 = 135$ K and $\Delta_2 = 498$ K as mentioned above. Δ_1 is much higher than T_{f}. At low temperatures, the Schottky specific heat can be ignored. C/T shows a maximum around T_{f}, then decreases with decreasing temperature. The $\gamma(0)$ estimated from the data below 1 K is 25 mJ/K^2 mol Ce (shown in the inset of Fig. 5). The heavy-fermion character is weak, which is also suggested by the slight increase of ρ at low temperatures. As recommended by Gschneider *et al.,* if normal heat capacity measurements give indications of heavy-fermion behavior, measurements should be extended to a temperature as low as possible. In this sense, the conclusion that the spin glass Ce_2AgSn_3 (Ref. 9) belongs to a heavy-fermion system is questionable.

In our transport measurements ρ and S, no anomaly was observed at T_{f}, which is common for a spin-glass system.[15] Here, we pay attention to the $S(T)$ curve of Ce_2NiGe_3. Although the absolute value is small in the temperature range of our measurement, it shows a similar structure as many other Ce-based antiferromagnetic Kondo compounds, such as CePdSn (Ref. 19) and $CeAl_2$ (Ref. 20). For these compounds the broad positive peak at high temperatures is due to the interplay of the Kondo effect and CEF effect.[21] The negative peak at low temperatures is attributed to the magnetic correlations.[19] This possibly applies to the present system as suggested from the result of the $-\ln T$-dependent magnetic resistivity and the CEF splitting energy levels. Fischer had calculated the thermoelectric power of spin glass on the basis of an s-d exchange model with additional interactions between the impurity spins by means of time-dependent perturbation theory.[14] The magnetic correlations result in a negative contribution to S. Combining with the positive Kondo term results in a sign change of S at a temperature T_0, which was crudely estimated to be the order of T_{f}. Thus, the negative peak at low temperatures could be considered as an indication of the existence of magnetic correlations as observed in antiferromagnet CePdSn,[19] in nonmagnetic heavy-fermion systems, $CeCu_2Si_2$ (Ref. 22) and $CeRu_2Si_2$,[23] and probably in the ferromagnet $CeGe_2$.[24]

In summary, the magnetism of Ce_2NiGe_3 was investigated. The results of magnetic susceptibility and specific heat indicated the formation of a spin-glass state below 3.5 K. In the paramagnetic range, the Kondo effect was observed in electrical resistivity and in thermoelectric power. Both frustration and disorder were found to play a crucial role for the formation of a spin-glass state. The γ value and resistivity at low temperatures suggest that the Kondo effect should get very weak in the spin-glass state. Neutron scattering experiments are desired to confirm the absence of long-range magnetic ordering and the information on the CEF splitting scheme obtained from specific heat.

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