Magnetic ordering in frustrated $Ce_5Ni_2Si_3$

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The transport, magnetic, and thermal properties are studied on an antiferromagnetic compound $Ce_5Ni_2Si_3$ with $T_N=7.3$ K. We find signatures of spin fluctuation in this geometrically frustrated magnet. The Curie-Weiss fit gives a large value of the paramagnetic Curie temperature, yielding a frustration parameter $f=8.4$. The electronic specific heat coefficient $\gamma=300$ mJ/Ce mol K^2 is strongly enhanced, leading to residual entropy at low temperatures. The spin fluctuation is suppressed as the magnetic field exceeds the metamagnetic transition field $H_m=1$ T, where the magnetoresistance decreases steeply. The steady increase of magnetic susceptibility below T_N is likely to be associated with the presence of paramagnetic Ce ions. For $La_5Ni_2Si_3$, a superconducting transition is observed at $T_c=1.8$ K.

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I. INTRODUCTION

The interesting physics provided by geometrically frustrated systems is under active discussion. The geometric frustration could be present as a part for some geometry of the network of spins and can come out with the nearest neighbor antiferromagnetic interactions. An appropriate geometry is as follows: (i) the triangular lattice made of triangles sharing an edge or the kagome lattice made of triangles sharing a vertex in two dimensions and (ii) the fcc lattice made of tetrahedra sharing an edge or that of the pyrochlore lattice made of tetrahedra sharing a vertex in three dimensions. The nearest neighbors of any spin in these lattices are themselves nearest neighbors of each other, which makes it intrinsically impossible to build a consistent antiferromagnetic configuration of collinear spins. A subset of spins exists for which there is no way to fix an orientation, which leads to infinitely degenerate manifolds of spin configurations differing from each other by local spin transformation. In general, the conditions for geometrical frustration are hard to meet in metallic crystals. The complexity of the interactions in metals makes a simple geometrical feature such as triangular coordination insufficient to induce frustration.

Nevertheless, physical properties of some special metals in the heavy fermion class of compounds have hallmarks of some of the geometrically frustrated magnets. For some geometrically frustrated systems like UNi_4B (Refs. 1–4) and CePdAl,[5] however, the novel antiferromagnetic ordering is discovered. The magnetic U atoms of UNi_4B occupy a triangular lattice in the basal plane and form a vertex structure with each vertex enclosing a nonmagnetic U ion, while the Ce atoms of CePdAl form a network having a kagome connection and show a mixed magnetic configuration.

Another candidate for the geometrically frustrated compounds with antiferromagnetic ordering could be $Ce_5Ni_2Si_3$. It crystallizes in the hexagonal Ce_2NiSi-type structure with a space group $P6_3/m$.[6] The crystal structure consists of complex trigonal prismatic assemblies build from small trigonal prisms with Ce atoms in the corners, as shown in Fig. 1. The unit cell is composed of four formula units. There are four inequivalent positions of Ce atoms, two inequivalent positions of Ni atoms, and one position of Si atoms. The prisms are filled with either Si or Ni atoms, which are ordered without any vacancies. The columns are infinite along z axis and they are limited within the xy plane, containing nine small trigonal prisms in the base of each column. In spite of such an interesting crystal structure, there has been no report on the physical properties of $Ce_5Ni_2Si_3$ so far. Isostructural system, $Pr_5Ni_{1.9}Si_3$, was intensively studied for its magnetic and thermal properties. Its magnetic moment orders ferromagnetically at $T_C=50$ K and undergoes a second antiferromagnetic transition at $T_N=25$ K, which is smeared out at $H>2$ T. In order to understand the novel magnetic phenomena occurring from the geometrical frustration in $Ce_5Ni_2Si_3$, we herein report details of its transport, magnetic, and thermal properties.

II. EXPERIMENT

Polycrystalline samples of $Ce_5Ni_2Si_3$ and $La_5Ni_2Si_3$ were prepared by an arc melting in an argon atmosphere and then annealed at 650 °C for 3 weeks in an evacuated quartz tube. Less than 0.2% weight loss occurred during the melting process. Metallographic analyses indicated that the samples used in this study are essentially single phased. The lattice parameters estimated from x-ray diffraction method are $a=15.997(9)$ Å and $c=4.309(1)$ Å for $Ce_5Ni_2Si_3$, and $a=16.210(8)$ Å and $c=4.352(1)$ Å for $La_5Ni_2Si_3$, which are well consistent with those in Ref. 6.

III. EXPERIMENTAL RESULTS

Figure 2(a) shows the temperature dependence of the magnetic contribution to the specific heat $C_m(T)$, which was estimated by subtracting the $C(T)$ data for $La_5Ni_2Si_3$ from those for $Ce_5Ni_2Si_3$. In zero field, $C_m(T)$ exhibits a pro-

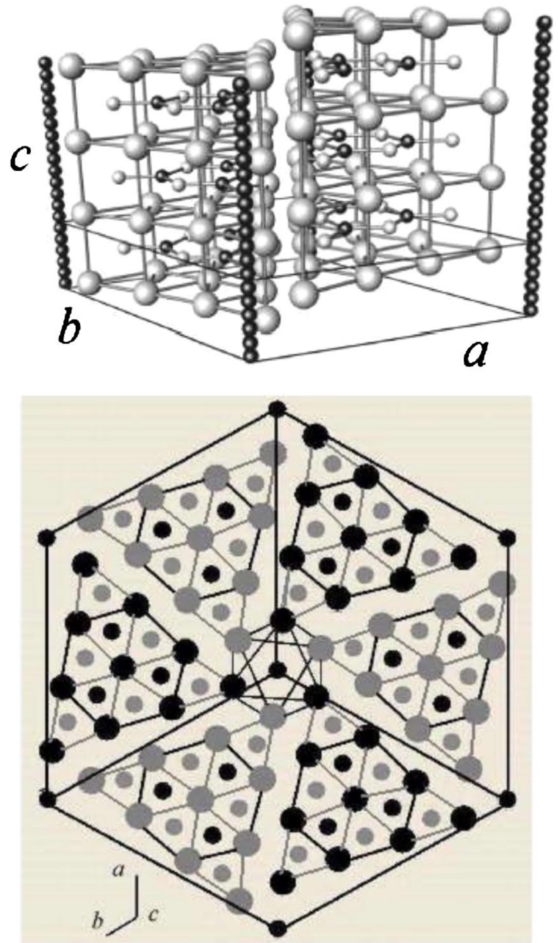

FIG. 1. Perspective (upper panel) (Ref. 7) and projective (lower panel) views of unit cell for $Ce_5Ni_2Si_3$. Ce atoms are represented by large gray and black circles, which are in the $c/4$ and $3c/4$ sites, respectively. Ni atoms are small black and Si atoms are small gray.

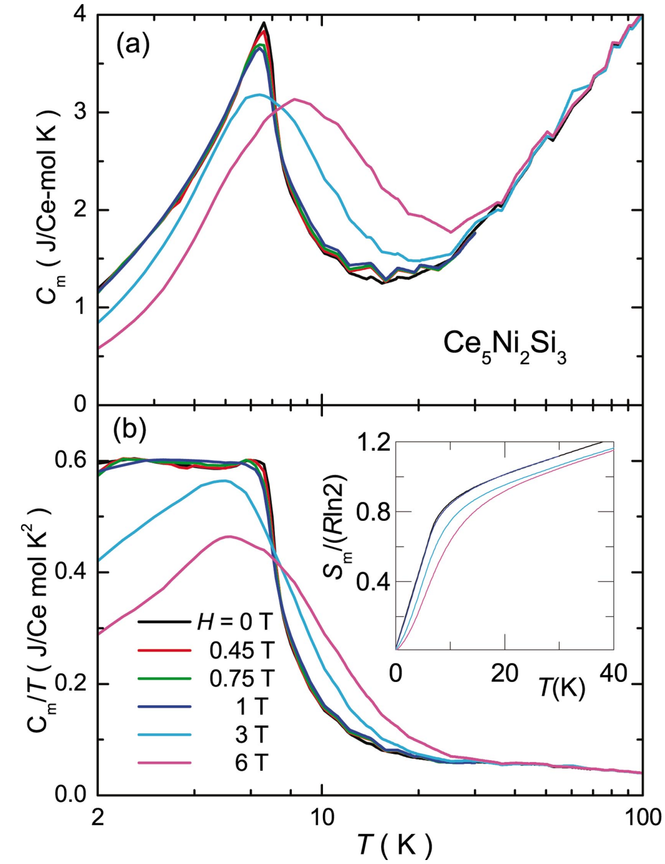

FIG. 2. (Color) (a) Magnetic contribution $C_m(T)$ to the specific heat and (b) C_m/T of $Ce_5Ni_2Si_3$ in various magnetic fields. Temperature dependence of the magnetic entropy $S_m(T)$ is plotted in the inset.

nounced peak centered at 6.6 K. The transition temperature T_N=7.3 K is defined by the midpoint of the jump in $C_m(T)$, which agrees with the antiferromagnetic ordering temperature observed in the magnetic susceptibility data. With increasing magnetic field up to 1 T, the peak temperature slightly moves down to 6.4 K for H=1 T, indicating that the magnetic ordering is indeed antiferromagnetic-type. However, further increase of the applied field results in a broad peak and the peak moves into higher temperatures. This implies that the magnetic ordering in fields exceeding 1 T is ferromagneticlike, which could be supported by the magnetization curve showing a field-induced ferromagnetic state above H_m=1 T. Above 30 K, the monotonic increase of $C_m(T)$ with temperature, independent of the applied magnetic field, is observed, which can be attributed to the crystalline-electric-field (CEF) effect. In the low temperature limit; see Fig. 2(b), one can find the linear Sommerfeld coefficient γ below 1 T away from the tail of a phase transition is roughly 300 mJ/Ce mol K^2, which is comparable to the γ value expected for the Kondo system. In our case of $Ce_5Ni_2Si_3$, using the value of paramagnetic Curie temperature θ_p=−61.3 K obtained from the Curie-Weiss fit of $\chi(T)$, the Kondo temperature is estimated to be $T_K \sim |\theta_p/2| \sim 31$ K, giving γ =190 mJ/Ce mol K^2 following the Coqblin-Schrieffer model.[8,9] It is noteworthy that the γ value obtained from the C_m/T curve is much larger than that estimated from the Curie-Weiss fit of $\chi(T)$. The proximity of the phase transition and the still elevated temperatures above 2 K introduces quite some uncertainty. In order to obtain the real γ value, we need to do the specific heat measurement at lower temperatures. Thus, there is other contribution to the large γ value in this system, which will be discussed in detail below. The large γ value gives rise to the large amount of entropy developing at low temperatures.

The inset of Fig. 2(b) displays the temperature dependence of magnetic entropy $S_m(T)$ normalized by the total entropy for Ce^{3+} doublet ground state, namely, $R\ln 2$ =5.76 J/Ce mol K. Clearly, there is seen large residual entropy. In zero field, $S_m(T)$ at T_N comes up to 0.55 $R\ln 2$. This reduced entropy could not be understood by considering the Kondo effect only. It reaches the full value of $R\ln 2$ around 20 K, which is comparable to the Kondo temperature T_K obtained from θ_p. The $S_m(T)$ curves are crossing at temperatures between T_N and T_K. This field variation of $S_m(T)$ seems to be associated with moderate competition between the ferromagnetic state and the Kondo state.

Figure 3(a) shows the temperature dependence of magnetic susceptibility $\chi(T)$ and its inverse $1/\chi(T)$ for

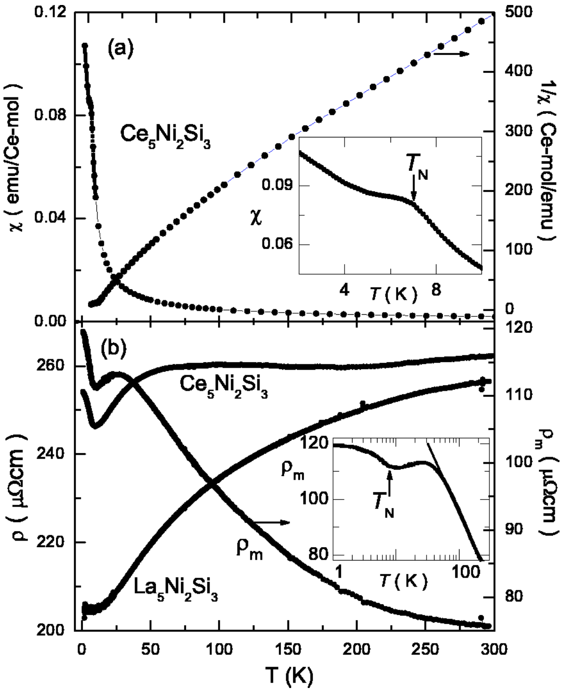

FIG. 3. (a) Temperature dependence of the magnetic susceptibility $\chi(T)$ and its inverse $1/\chi(T)$ for $Ce_5Ni_2Si_3$ measured at $H = 100$ G. The inset shows the low temperature data of $\chi(T)$. (b) Temperature dependence of the electrical resistivity $\rho(T)$ for $Ce_5Ni_2Si_3$ and $La_5Ni_2Si_3$. The resistivity of $La_5Ni_2Si_3$ shifts to a positive direction by 70 $\mu\Omega$ cm. The magnetic contribution ρ_m to the electrical resistivity of $Ce_5Ni_2Si_3$ is also plotted. The inset shows the low temperature data of ρ_m.

$Ce_5Ni_2Si_3$. It is found that $\chi(T)$ increases with decreasing temperature and exhibits an anomaly due to an antiferromagnetic ordering at $T_N = 7.3$ K. As seen in the inset of Fig. 3(a), $\chi(T)$ still increases below T_N, which is not expected for a normal antiferromagnet. Such a Curie tail below T_N, which is also observed in $\chi(T)$ of UNi_4B (Ref. 1) and $CeSn_3$,[10] is independent of the applied magnetic field and thus is likely intrinsic property of the compound rather than an impurity effect. At temperatures above 150 K, $1/\chi(T)$ follows the Curie-Weiss law with an effective magnetic moment $\mu_{\rm eff} = 2.42\ \mu_B/\mathrm{Ce}$ and a paramagnetic Curie temperature $\theta_p = -61.3$ K. The estimated value of $\mu_{\rm eff}$ is comparable to the theoretical value of 2.54 μ_B/Ce for a free Ce^{3+} ion, indicating that the magnetic moment of Ce ions is localized and the Ni ions do not carry magnetic moments. The observed negative sign of θ_p can be understood to arise from the development of antiferromagnetic-type correlations between the Ce moments at high temperatures. The relatively large value of θ_p might be associated with the Kondo effect or the frustrated magnetic moments, which will be discussed below. At temperatures below 150 K, the deviation from the Curie-Weiss behavior could be attributed to the CEF effect. More experiments such as high-resolution angle-resolved photoemission studies and inelastic neutron scattering measurements are required to estimate the CEF parameters.

The temperature dependence of electrical resistivity $\rho(T)$ for $Ce_5Ni_2Si_3$ and $La_5Ni_2Si_3$ is plotted in Fig. 3(b), together

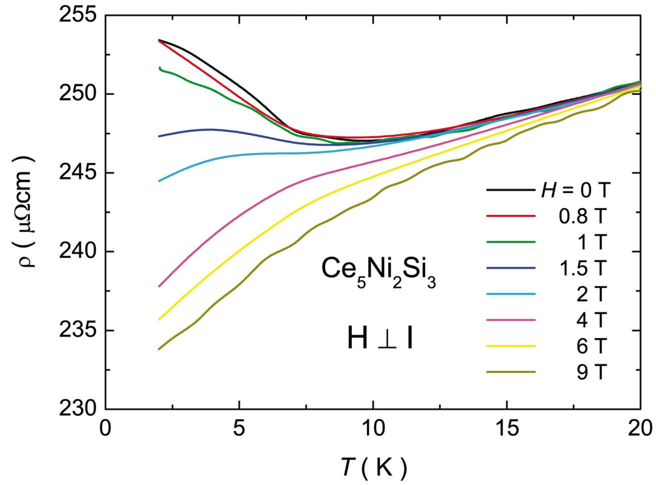

FIG. 4. (Color) Temperature dependence of the electrical resistivity $\rho(T)$ measured at various magnetic fields for $Ce_5Ni_2Si_3$.

with the magnetic resistivity given by $\rho_m = \rho(Ce_5Ni_2Si_3) - \rho(La_5Ni_2Si_3)$. It is found that $\rho(T)$ of $Ce_5Ni_2Si_3$ decreases monotonically with temperature down to 100 K and exhibits an upward curvature around 50 K and eventually increases sharply below 10 K. The sharp rise in $\rho(T)$ just below T_N is often found in rare-earth intermetallic compounds showing spin density waves, superzone gap, and spin fluctuation,

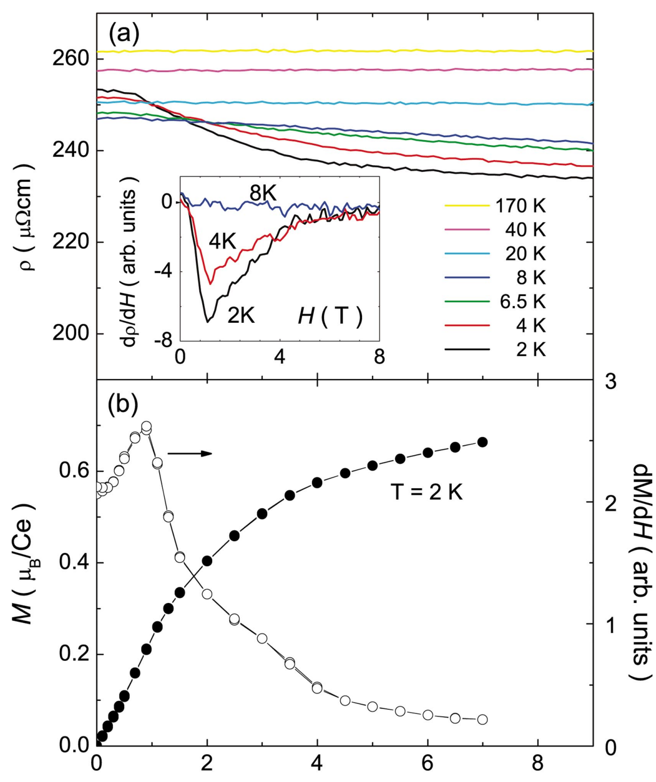

FIG. 5. (Color) (a) Magnetic field dependence of the electrical resistivity $\rho(H)$. The field derivatives of the electrical resistivity $d\rho/dH$ at various temperatures are plotted in the inset. (b) Magnetic field dependence of the magnetization $M(H)$ and the field derivative dM/dH at $T = 2$ K for $Ce_5Ni_2Si_3$.

which will be discussed later. The residual resistivity is obtained to be about 245 $\mu\Omega$ cm. Such a high residual resistivity could be associated with an impurity effect and/or crystalline anisotropy. On the other hand, $\rho(T)$ of $La_5Ni_2Si_3$ decreases with decreasing temperature as a usual metal and exhibits a superconducting transition at $T_c=1.8$ K. In the inset of Fig. 3(b), the magnetic contribution $\rho_m(T)$ to the electrical resistivity of $Ce_5Ni_2Ge_3$ shows a semi-log T behavior in the high temperature region, which is attributed to the Kondo effect considering the CEF effect.

We have further studied the magnetic field effect on the transport and magnetic properties of $Ce_5Ni_2Si_3$ by measuring magnetoresistance and magnetization. Figure 4 shows $\rho(T)$ with varying magnetic fields up to 9 T perpendicular to the current. The sharp rise in $\rho(T)$ just below T_N is suppressed as the field is increased. In fields above 2 T, no anomaly is noticed at temperatures down to 2 K. Such a negative magnetoresistance is remarkable at low temperatures below T_N. The field dependence of resistivity $\rho(H)$ at constant temperatures is presented in Fig. 5(a), together with the field derivative $d\rho/dH$ in the inset. At temperatures below T_N, $\rho(H)$ decreases steeply around $H_m=1$ T and tends to saturate in higher magnetic fields. On the other hand, $\rho(H)$ above T_N is independent of the applied field. These results agree with the metamagnetic transition observed in the magnetization data. Figure 5(b) shows the isothermal magnetization $M(H)$ measured at 2 K. It is found that $M(H)$ deviates upward from the linear dependence around H_m and exhibits partial saturation at higher fields. No complete saturation, as seen in $\rho(H)$, is observed up to 7 T. The value of magnetic moment at 7 T is 0.66 $\mu_B/$Ce, which is much less than the full moment expected from a free Ce^{3+} ion. This might be associated with the Kondo and/or CEF effects considering crystallographic anisotropy. The plot of field derivative of the magnetization dM/dH exhibits a sharp peak around $H_m=1$ T due to the metamagnetic transition, which is probably of the spin-flip type, from the antiferromagnetic ground state to a field-induced ferromagnetic state. It is worthwhile mentioning that this field value coincides with H_m where $d\rho/dH$ exhibits a sharp peak.

IV. DISCUSSION

We discuss below the unusual dynamics of magnetic correlations in $Ce_5Ni_2Si_3$, which could be explored by considering spin density wave, superzone gap, or spin fluctuation, as mentioned above. For materials with spin density wave or superzone gap, the physical properties can be understood to arise from the development of partially gapped Fermi surface at the Fermi level. Because of the energy gap, $\rho(T)$ is steeply increased just below T_N and is strongly suppressed by applying magnetic field. In addition, C_m/T in such systems approaches zero as the temperature is decreased below T_N. For $Ce_5Ni_2Si_3$, however, it rather increases as approaching $C_m/T(T\rightarrow 0)=300$ mJ/Ce mol K^2. In addition, the slope of the measured $1/\chi(T)$ curve yields a large value of θ_p, resulting quantitatively in the frustration parameter $f=-\theta_p/T_N=8.4$. Such large γ and f values are often observed in materials with geometrical frustration.[11–13] The spin fluctuation due to the geometrical frustration is responsible to the rapid rise of $\rho(T)$ just below T_N and its suppression in field.

Compared to rather relatively simple crystal structure and magnetic correlations of UNi_4B and CePdAl,[1–5] the unit cell of $Ce_5Ni_2Si_3$ consists of four formula units with twenty Ce atoms and the magnetic correlations are complex. Twelve Ce atoms in two hexagons, two Ce atoms lying inside the hexagon, and six Ce atoms forming two triangular lattices. At $T_N=7.3$ K, 12/20 of the magnetic Ce ions in two hexagons seems to order into an antiferromagnetic pattern in the basal plane, because the in-plane Ce-Ce distance is shorter that the interplane Ce-Ce distance and thus the magnetic ordering is expected to occur in the basal plane. Then, the magnetic interaction around the antiferromagnetically ordered Ce ions in the hexagonal arrangement might be cancelled out, resulting that 2/20 of the spins lying inside the hexagon are paramagnetic. The presence of the paramagnetic state that incorporates with the antiferromagnetic ordering could give rise to the steady increase in $\chi(T)$ below T_N as well as the upturn in $\rho(T)$ just below T_N. The remaining 6/20 of the spins with having two triangles as the structural unit seem to be of the frustrating type. Even above $H_m=1$ T, there are possibly two types of magnetic correlations as the structural unit corresponding to the hexagonal structure into an antiferromagnetic pattern and the triangular structure into a field-induced ferromagnetic pattern, in addition to the background of paramagnetic state. In this sense, we are able to understand the negative slope of $\rho(H)$ below T_N as the result of reduced magnetic scattering by polarizing the fluctuating spins which occupy the triangular lattices.

These are only qualitative observations for the experimental signatures of geometrical frustration in $Ce_5Ni_2Si_3$. To illustrate this point, further studies such as neutron scattering and μSR experiments are needed. Of particular interest in future directions is to study the single crystal of $Ce_5Ni_2Si_3$, which will provide us to identify this system that possess strong geometrical frustration and to address the crystallographic anisotropy that is important in such a frustrating compound. Another system of interest is the substituted system $Ce_{5-x}La_xNi_2Si_3$, which will allow us to control disorder. If the triangular lattice is replaced by a random lattice, then spin-glass behavior can be driven by introducing disorder. Substitution of La for Ce may induce negative chemical pressure and then the antiferromagnetic state may be presumably destabilized. In addition, the application of external pressure could suppress the spin fluctuation. Such studies will provide a different way to realize a system of strongly interacting spins with random quenched disorder.

V. CONCLUSION

In conclusion, we have studied the transport, magnetic, and thermal properties of $Ce_5Ni_2Si_3$. We find the antiferromagnetic transition at $T_N=7.3$ K but a relatively large value of $\theta_p=-61.3$ K from the well-defined Curie-Weiss fit, giving a frustration parameter $f=8.4$. The low-temperature data of $C_m(T)$ yields a sufficiently large residual entropy with $\gamma=300$ mJ/Ce mol K^2. These experimental signatures of geometrical frustraction in $Ce_5Ni_2Si_3$ could be understood by considering the special geometry of the lattices without introducing disorder. The magnetic Ce ions which order into an antiferrromagnetic pattern form hexagonal nets in the basal plane, the paramagnetic Ce ions lie in the center of each hexagon, and the remaining Ce ions which may be geometrically frustrated occupy the triangular lattice.

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