Kondo ground state of $CeCoGe_2$ with $j=\frac{5}{2}$

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We report results for the magnetic susceptibility, specific heat, and electrical resistivity of $CeCoGe_2$, which shows a heavy-fermion-like behavior with the Kondo temperature scale $T_K \sim 250$ K. The Ce ion in this compound turns out to be in the normal trivalent state, compared with valence fluctuation in the previous study for a nonstoichiometric sample of $CeCo_{0.89}Ge_2$. The presented results of $CeCoGe_2$ are well interpreted by the Coqblin-Schrieffer model with $j=5/2$ ground state for heavy-fermion Kondo systems.

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I. INTRODUCTION

Ternary intermetallic compounds of $CeTX_2$ (T=transition metals and X=semiconducting elements) are the subject of continuous interest because they show a wide variety of ground states, such as heavy-fermion behavior in $CePtSi_2$,[1] valence fluctuating behavior in $CeRhSi_2$,[2] heavy-fermion ferromagnetic behavior in $CeRuSi_2$,[3] nonmagnetic valence fluctuating behavior in $CeNiSi_2$,[4] and antiferromagnetic Kondo lattice behavior in $CeNiGe_2$.[5] The nature of the ground state depends strongly on the strength of the hybridization. In an effort to search the ternary system of $CeCoGe_2$, there has been a previous study only for a nonstoichiometric sample of $CeCo_{0.89}Ge_2$ so far,[6] reporting a heavy-fermion valence fluctuating behavior. This compound has a rather large electronic specific-heat coefficient $\gamma = 128$ mJ/mol K^2. The magnetic ordering is observed to be absent at temperatures down to 1.5 K. The valence fluctuation behavior is suggested with an effective valence of Ce ion varying between 3+ and 4+, which was obtained from a simple model for the magnetic susceptibility of rare-earth compounds exhibiting valence fluctuations by Sales and Wohlleben.[7] However, the Sales-Wohlleben model has a fair fit of our experimental data only in the temperature range from 60 K to 280 K. In order to understand the nature of the ground state of concentrated Kondo compound $CeCoGe_2$, we herein report further details of this interesting Kondo compound.

II. EXPERIMENT

Polycrystalline samples of $CeCoGe_2$ and $LaCoGe_2$ were prepared by arc melting in an argon atmosphere and then annealed at 900 °C for three weeks in an evacuated quartz tube. The purities of the starting materials were 99.9% for Ce(La), 99.99% for Ni, and 99.9999% for Ge. Less than 0.3% weight loss occurred during the melting process. Metallographic analyses indicated that the samples used in this study are single phased. A powder x-ray diffraction pattern revealed them to crystallize in the orthorhombic $CeNiSi_2$-type (space group $Cmcm$) structure. The lattice parameters are $a=4.258(1)$ Å, $b=16.787(6)$ Å, and $c=4.215(3)$ Å for $CeCoGe_2$, and $a=4.307(0)$ Å, $b=16.845(6)$ Å, and $c=4.245(7)$ Å for $LaCoGe_2$. The magnetic susceptibility was measured using a quantum design superconducting quantum interference device magnetometer from 1.8 K to 300 K at $H=1000$ G. The specific heat was taken by a relaxation method with a physical property measurement system from 1.8 K to 160 K. The electrical resistivity was measured by the conventional dc four-probe method from 0.5 K to 300 K with a ^{3}He refrigerator. In order to eliminate the errors which can occur on measuring dimensions of samples, the measured resistivity is corrected by that measured by Van der Pauw method at 300 K.

III. RESULT AND DISCUSSION

A. Magnetic susceptibility

Figure 1 displays the temperature dependence of the magnetic susceptibility $\chi(T)$ and its inverse $1/\chi$ of $CeCoGe_2$. In the temperature range from 300 K to 200 K, $1/\chi$ is linear to temperature and is successfully fitted with the Curie-Weiss law, from which we could obtain the paramagnetic Curie

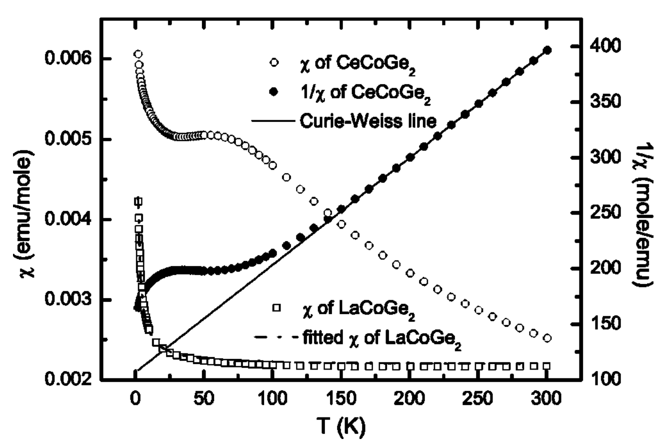

FIG. 1. Magnetic susceptibility $\chi(T)$ and its inverse $1/\chi$ for $CeCoGe_2$ and $LaCoGe_2$. The data of $LaCoGe_2$ are shifted by 0.002 emu/mole for better display. The solid line is a fitting curve by the Curie-Weiss term with a temperature-independent susceptibility $\chi_0 = 2.1\times10^{-4}$ emu/mol and the dash-dotted line is a curve by the Curie law plus $\chi_0 = 1.8\times10^{-4}$ emu/mol.

temperature of $\theta_P = -69.(7)$ K and the effective magnetic moment of $\mu_{eff} = 2.69(2)\ \mu_B$. The large negative value of θ_P is presumed to be due to a high Kondo temperature T_K. The value of μ_{eff} is a little larger than 2.54 μ_B of a free-ion value of Ce^{3+}. Thus, we have tried to analyze the χ data with the Curie-Weiss law involving a temperature-independent term χ_0, which might stem from the temperature-independent Van Vleck, conduction-electron paramagnetic, and core-electron diamagnetic contributions. In this case, we could estimate $\chi_0 = 2.5(0) \times 10^{-4}$ emu/mol, $\theta_P = -65.(3)$ K, and $\mu_{eff} = 2.55(4)\ \mu_B$. The value of μ_{eff} is equal to that of a free Ce^{3+} ion. This implies that the valence of Ce ion in $CeCoGe_2$ is an integer at high temperatures. This result is certainly different from the preliminary study reported by Pecharsky *et al.*[6] We find that $\chi(T)$ tends to saturate at lower temperatures below the faint maximum around 60 K and exhibits the upturn in the lowest temperature region below 20 K, which is often observed in Ce compounds with high Kondo temperatures.[8] Since the magnetic moment of these compounds is compensated by the conduction electrons in the temperature region lower than the Kondo temperature and then is small compared with that of the compounds with low Kondo temperature, a small amount of impurity or inhomogeneity can form the upturn at low temperatures. In order to understand the origin of this upturn in $CeCoGe_2$, we have measured $\chi(T)$ of $LaCoGe_2$. It is found that $\chi(T)$ of $LaCoGe_2$ above 50 K is almost independent of temperature. Below 20 K, $\chi(T)$ increases with decreasing temperature, similar to that of $CeCoGe_2$. Since the increasing ratio of $\chi(T)$ at low temperatures is dependent on the annealing condition of the sample, we consider that this increase comes from the misplacement of a small amount of Co ions from their correct crystallographic positions. The increase is analyzed by fitting with the Curie law and thus it can be interpreted by assuming that only 0.13 at. % Co is magnetic with a full magnetic moment of 4.8 μ_B as an external parameter. The calculated result is also plotted in Fig. 1 as the dash-dot line. In the same manner, the upturn in $CeCoGe_2$ is also understood in a way similar to that of $LaCoGe_2$, probably due to the misplacement of a small amount of Ce and/or Co ions from the correct crystallographic positions. Supposing that only Co ions contribute to the upturn of $\chi(T)$ at low temperatures in $CeCoGe_2$, we could obtain that 0.08 at. % Co is magnetic in $CeCoGe_2$.

In Fig. 2, $\chi(T)$ for $CeCoGe_2$ is corrected by the same method to $LaCoGe_2$. It is worthwhile to mention here that the weak peak observed at 60 K is more clearly revealed after the correction and that $\chi(T)$ saturates toward $\chi(0) = 4.26 \times 10^{-3}$ emu/mol, as usually found for Kondo materials. We consider that the peak may be a result of the orbital effect of total angular momentum j larger than 1/2, as proposed by Coqblin and Schrieffer.[9] In the Coqblin-Schrieffer model, the spin-orbit exchange scattering is taken into account for the Kondo effect caused by Ce ions. Hence, in this model the multiplicity $2j+1$ for the total angular momentum plays an important role in stabilizing the Kondo state and raising T_K. The Kondo impurity problem in the Coqblin-Schrieffer model has been numerically calculated for several total angular momenta by Rajan.[10] The same characteristic temperature $T_0 = 230$ K is used for all the j values, since the calculated result is the best fit to the eyes. The result of this calculation is drawn in Fig. 2, in addition to the corrected $\chi(T)$ data of $CeCoGe_2$. The curves for $j=1/2$ and $j=3/2$ cannot be fitted in $\chi(T)$, but that for $j=5/2$ can be. This implies that the total angular momentum of $CeCoGe_2$ contributing to the Kondo effect at $T < T_K$ could be $j=5/2$, which will be confirmed in the following analysis of specific heat. The Kondo temperature T_K is calculated to be 280 K using the value of $T_0 = 230$ K. We can alternatively estimate T_K from $\chi(0) = 4.26 \times 10^{-3}$ emu/mol using the following relation:

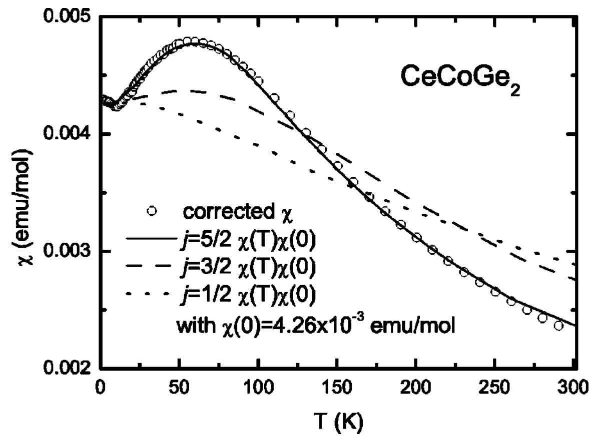

FIG. 2. Corrected $\chi(T)$ of $CeCoGe_2$ by using the method mentioned in the text. The calculated results from the Coqblin-Schrieffer model are also included; the dotted line is for $j=1/2$, the dashed line is for $j=3/2$, and the solid line is for $j=5/2$ with $T_0 = 230$ K.

$$T_K^{\chi(0)} = \frac{\nu(\nu^2-1)\mu_B^2 g^2 W}{24\pi k_B \chi(0)},$$

where $\nu = 2j+1 = 6$, $g = 6/7$, and W is the Wilson number $0.1026 \times 4\pi$, and consequently we obtain 233 K.

B. Specific heat

The specific heat $C(T)$ data of both $CeCoGe_2$ and $LaCoGe_2$ from 1.8 K to 160 K are shown in Fig. 3. No anomaly due to a long-range magnetic order for $CeCoGe_2$ is found in the measured temperature region. The temperature-linear term γ and the Debye temperature of $LaCoGe_2$ are 7.1 mJ/mol K^2 and 220 K, respectively. The magnetic specific heat C_m was estimated by subtracting the $C(T)$ data of $LaCoGe_2$ from those of $CeCoGe_2$. The result is plotted in Fig. 4. The most striking feature is that C_m has a broad peak around 70 K. This peak might be explained by the Schottky anomaly due to the crystal-field splitting. For $CeCoGe_2$, $j=5/2$ state splits into three doublets considering the crystal field with the orthorhombic symmetry. However, we find that the peak of the Schottky anomaly is too narrow to fit the measured data if we try

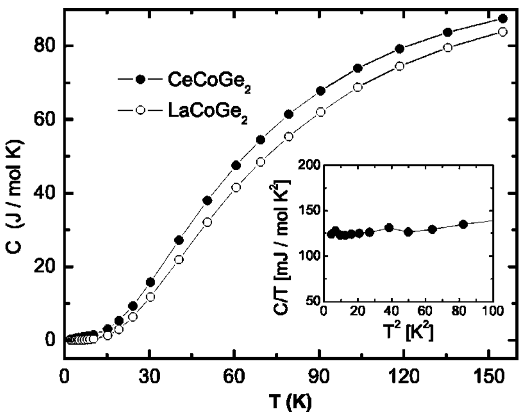

FIG. 3. Specific heats $C(T)$ for both $CeCoGe_2$ and $LaCoGe_2$. The inset shows the result of C/T vs T^2.

to make the best fit considering the height. On this account, we believe that the broad peak is generated by the formation of the Kondo resonance peak near the Fermi level since $\chi(T)$ is well understood by the Coqblin-Schrieffer model. The C_m curves calculated from the Coqblin-Schrieffer model[10] are also displayed in Fig. 4, together with the crystal-field fit. As a fitting parameter, we used the characteristic temperature $T_0=90$ K for $j=1/2$, 160 K for $j=3/2$ and 220 K for $j=5/2$ in this calculation because we tried that the peak temperature of the experimental C_m is same as that of the calculated C_m. The calculated C_m values for $j=1/2$ and $j=3/2$ are obviously too far from the measured C_m, but that for $j=5/2$ agrees well. We come to the conclusion that the Coqblin-Schrieffer model with $j=5/2$ reasonably explains thermal excitation of both $\chi(T)$ and $C(T)$ of $CeCoGe_2$. From this analysis, T_K is evaluated to be 283 K, which is in fair agreement with that obtained from $\chi(T)$. The temperature-linear term γ of the conduction-electron contribution is as large as 123 mJ/mol K^2, which is demonstrated in the inset of Fig. 3. In the Coqblin-Schrieffer model,[9,10] T_K can be estimated from γ by the following equation:

$$T_K^{\gamma}=\frac{Wj\pi R}{3\gamma},$$

where R is the gas constant. We find $T_K=228$ K for $j=5/2$ from $\gamma=123$ mJ/mol K^2, in good agreement with those estimated from the analyses by the Coqblin-Schrieffer model mentioned above.

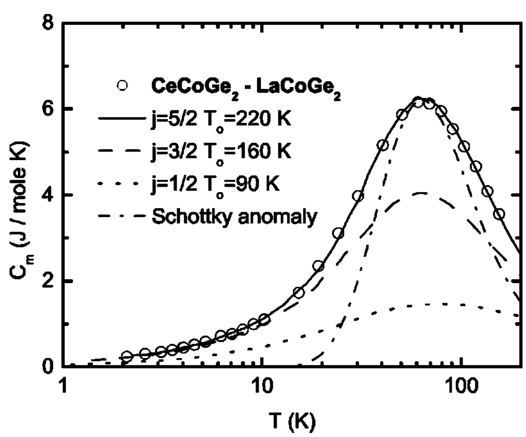

FIG. 4. Magnetic specific heat C_m of $CeCoGe_2$, together with the calculated C_m curves by the Coqblin-Schrieffer model with $T_0=90$ K for $j=1/2$ (dotted line), $T_0=160$ K for $j=3/2$ (dashed line), and $T_0=220$ K for $j=5/2$ (solid line). C_m calculated by the Schottky anomaly with three doublets is also included as the dash-dotted line. In this calculation, the splitting energies of the first excited and the second excited doublets from the ground state are 150 K and 190 K, respectively.

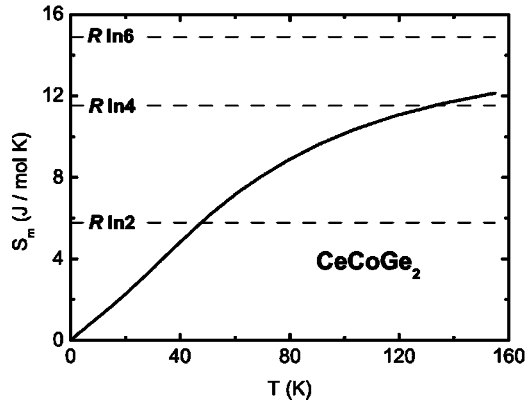

FIG. 5. Magnetic entropy S_m for $CeCoGe_2$.

The magnetic entropy S_m is calculated by integrating C_m/T with respect to T and is plotted in Fig. 5. With increasing temperature up to 20 K, S_m is proportional to the temperature. Its slope is relatively large to be about 120 mJ/mol K^2 and is nearly equivalent to the above γ value. Above 50 K, S_m bends downward and reaches 12.2 J/mol K at 160 K, which is larger than $R\ln 4=11.5$ J/mol K. This fact implies that there would be no more magnetic phase transition below the limit of the temperature range of the present $C(T)$ measurement. If there is additional magnetic phase transition at lower temperatures, the entropy of $R\ln 2$ due to the transition should be added in S_m because the ground state with tetragonal symmetry is a doublet. In that case, S_m at 160 K exceeds $R\ln 6=14.9$ J/mol K of the full entropy for the Ce^{3+} ion with $j=5/2$. In fact, we observe no phase transition down to 0.5 K in the transport measurements with a ^{3}He refrigerator. The full entropy of $R\ln 6$ seems to be reached around 350 K, which is larger than T_K estimated above, since the total angular momentum degrees of freedom are released when the thermal bath overcomes T_K.

C. Electrical resistivity

The electrical resistivity $\rho(T)$ of $CeCoGe_2$ is shown with that of $LaCoGe_2$ in Fig. 6. $\rho(T)$ of $CeCoGe_2$ remains constant at high temperatures and shows a sudden decrease below 80 K, while $LaCoGe_2$ demonstrates an ordinary metallic behavior, of which $\rho(T)$ is linearly dependent on temperature due to the phonon scattering at high temperatures. The difference in $\rho(T)$ between the two compounds should have a magnetic origin. The temperature dependence of the magnetic contribution to the electrical resistivity ρ_m, defined as

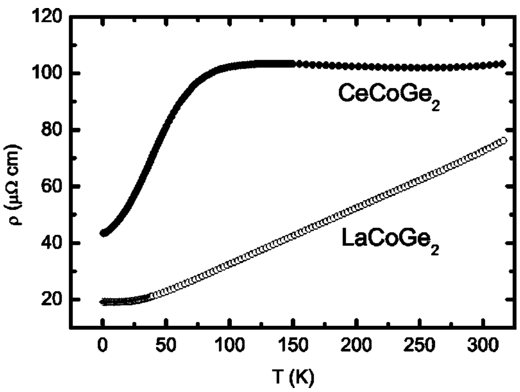

FIG. 6. Electrical resistivity $\rho(T)$ of both $CeCoGe_2$ and $LaCoGe_2$.

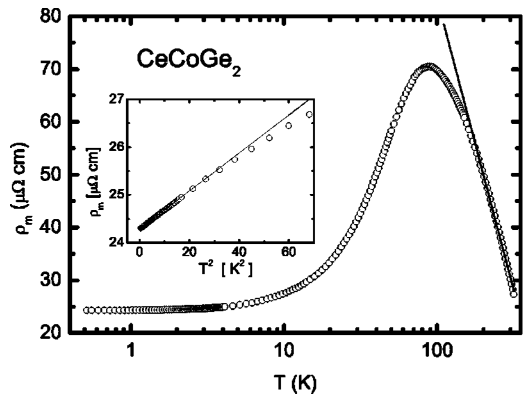

FIG. 7. Magnetic resistivity ρ_m for $CeCoGe_2$ as a function of logarithmic scale of temperature. The inset shows the T^2 dependence of ρ_m in the low-temperature region.

$\rho(CeCoGe_2)$-$\rho(LaCoGe_2)$, is plotted in Fig. 7. It is found that ρ_m has a broad peak around 90 K and decreases logarithmically at the temperature region between 200 K and 300 K. This linear behavior is expected for a typical Kondo scattering. The relatively sharp decline on the low-temperature side of the peak should be attributed to the coherence characteristic of a Kondo lattice. The broad peak of ρ_m is qualitatively understood as a Kondo effect influenced by the crystal-field splitting as was first calculated by Cornut and Coqblin.[11] As mentioned in the above section, the large T_K value in $CeCoGe_2$ reflects that crystal field is expected to play a secondary role and the broad peak is due to the Kondo effect of the total $4f$ degrees of freedom with $j=5/2$. Below 5 K, a quadratic temperature dependence $\rho_m = AT^2$ is observed, being a characteristic feature predicted by Fermi-liquid state for heavy electron Kondo systems. The coefficient of a quadratic term A is relatively small as 0.0397 $\mu\Omega$cm/K^2. This result means that $CeCoGe_2$ forms the coherent Fermi-liquid state even at high temperatures. It should be noted that most Kondo compounds exhibit the T^2 dependence of ρ_m well below 1 K. Recently, it has been reported that ρ_m of $CeFeGe_3$ with $T_K = 230$ K has a T^2 dependence up to 5 K.[11] This feature seems to be a characteristic of compounds with high Kondo temperature.

For a heavy-electron system, there exist correlations among some parameters such as the enhanced γ, $\chi(0)$, and A. The Wilson ratio R_w among these correlations is estimated to be 1.17 for $CeCoGe_2$, which fits fairly well among those of other heavy-electron compounds.[12] The Kadowaki-Woods relation A/γ^2 is calculated to be 2.6×10^{-6} $\mu\Omega$cm mol^2 K^2/m J^2 and also agrees with those of other heavy-electron compounds.[13]

D. $j=\frac{5}{2}$ Kondo state

As discussed above, $CeCoGe_2$ is a $j=5/2$ Kondo compound with a high Kondo temperature of the order of 200 K. The phenomena similar to $CeCoGe_2$ have been observed in $CePd_3$, $CeSn_3$, and CeNi, which are the intermediate-valence compounds having a higher T_K than 200 K.[8] These intermediate-valence compounds possess a noninteger valence at room temperature as a result of stronger hybridization of $4f$ with conduction electrons, because of the anomalous proximity of the $4f$ level to the Fermi level. On the contrary, $CeCoGe_2$ is trivalent at high temperatures and is well interpreted by the Coqblin-Schrieffer model with $j=5/2$, which is an integer-valent impurity Kondo model. This implies that the sixfold degenerate states without the crystal-field splitting form the Kondo state. In most of Ce-based Kondo compounds studied in detail up to now, except $CeFeGe_3$,[12] T_K is smaller than the crystal-field splitting energy. In $CeFeGe_3$, T_K is the order of crystal-field splitting and $j=3/2$ Kondo model is well fitted.[12] $CeCoGe_2$ among Ce compounds is most likely to be the first Kondo system clearly interpreted by the Coqblin-Schrieffer model with $j=5/2$.

IV. CONCLUSION

Experimental results for the magnetic, thermal, and transport properties show that $CeCoGe_2$ is a nonmagnetic heavy-fermion Kondo compound with $T_K > 200$ K. The magnetic susceptibility saturates into $\chi(0)=4.26\times10^{-3}$ emu/mol followed by a maximum around 60 K and above 200 K it satisfies the Curie-Weiss law with $\mu_{eff}=2.55\ \mu_B$ and $\theta_P = -65.3$ K. The heavy-fermion-like behavior is found in the specific heat with a rather large Sommerfeld coefficient $\gamma = 123$ mJ/mol K^2 well below 70 K, where there appears a broad peak. We observe a T^2 dependence of the electrical resistivity below 5 K and a coherence characteristic of the Kondo lattice around 90 K. These results are excellently consistent with the Coqblin-Schrieffer Kondo model with $j=5/2$ for $CeCoGe_2$. Thus, the present system could give a unique opportunity for studying the nature of $j=5/2$ ground state for heavy-fermion Kondo systems.

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