Coexistence of localized and heavy itinerant states in antiferromagnetic $CePtGe_2$

Tomohito Nakano,[1,*] Shoma Onuma,[1] Naoya Takeda,[2] Klára Uhlířová,[3] Jan Prokleška,[3] Vladimír Sechovský,[3] Jun Gouchi,[4] and Yoshiya Uwatoko[4]

[1]*Graduate School of Science and Technology, Niigata University, Ikarashi, Niigata 950–2181, Japan*
[2]*Faculty of Engineering, Niigata University, Ikarashi, Niigata 950–2181, Japan*
[3]*Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech*
[4]*ISSP, University of Tokyo, Kashiwa, Chiba 277–8581, Japan*

(Received 6 November 2018; revised manuscript received 6 June 2019; published 9 July 2019)

Two conflicting ground states, i.e., an antiferromagnetic ground state at 3.8 K and a ferromagnetic ground state at 5.1 K, have been reported for $CePtGe_2$, which has two nonequivalent crystallographic Ce sites. In this study, we have prepared polycrystalline and single-crystalline $CePtGe_2$ samples and measured their magnetization, specific heat, resistivity, and Seebeck coefficient. The observed bend in resistivity, peak in magnetic susceptibility, and λ-type anomaly in specific heat at $T_N = 3.8$ K and the metamagnetic transition in this $CePtGe_2$ suggest antiferromagnetism at low temperatures. No evidence of ferromagnetic order was found in the studied temperature range, indicating possible crystal polymorphism with ferromagnetic character. The large susceptibility around T_N and the Schottky-type specific heat indicate a well-localized f-electron state. However, the large residual γ and $\chi(0)$ indicate an itinerant heavy f-electron state. These findings suggest the coexistence of localized and heavy itinerant states corresponding to f electrons at the two Ce sites in this antiferromagnetic $CePtGe_2$. The field dependence of magnetization indicates a sudden increase in magnetization at weak magnetic fields (∼0.2 T), followed by a plateau at fields above 0.2 T, resulting in a possible different polarized metamagnetic state via interaction between localized and itinerant f electrons.

DOI: 10.1103/PhysRevB.100.035107

I. INTRODUCTION

In the field of condensed matter physics, the degrees of freedom of d and f electrons resulting from their valence, orbital, and spin are known to be related to various important phenomena, including magnetic [1–3], valence [4,5], multipole [6–8], superconducting [9–11] order and transitions, multiferroic [12,13] and thermoelectric [14,15] effects, and magnetoresistance [16]. Ce^{3+}-based compounds, which are the simplest f-electron system, have been studied by many researchers since the discovery of the unconventional superconductivity of heavy quasiparticles in $CeCu_2Si_2$ in 1979 [17,18]. Although numerous studies have focused on Ce compounds with one equivalent crystallographic Ce site, many multisite Ce compounds exist such as $Ce_2Ni_{12}P_7$ and $Ce_3Pd_{20}Si_6$ [19,20]. Multiple local situations/conditions (e.g., symmetry) allow us to expect different types of intersite interactions and fluctuation and different types of phenomena. The compound studied herein, $CePtGe_2$, has two equivalent Ce sites and may possess interesting phenomena.

$CePtGe_2$ has a $YIrGe_2$-type orthorhombic crystal structure in the space group *Immm* [as shown in Fig. 1(a)] with lattice constants $a = 4.428$, $b = 16.48$, and $c = 8.795$ Å. This structure includes two crystallographically nonequivalent Ce sites, $4i$(Ce 1) and $4h$(Ce 2), with point symmetries $mm2$ and $m2m$, respectively. Pecharsky *et al.* [21] reported the physical properties of this compound using polycrystalline samples. They found that $CePtGe_2$ shows an antiferromagnetic/ferrimagnetic transition at $T = 3.8$ K, as evidenced by a jump in specific heat, a bend in resistivity, and an antiferromagnetic peak in susceptibility. The authors also reported a metamagnetic-like transition in magnetization at 0.2 T. In contrast, based on polycrystals and single crystals, Kirita *et al.* [22] observed a clear ferromagnetic anomaly at 5.1 K based on specific heat, resistivity, and susceptibility. Thus, contrasting results have been reported for $CePtGe_2$. In this study, we have clarified the intrinsic properties of antiferromagnetic/ferrimagnetic $CePtGe_2$, which has two crystallographically nonequivalent Ce sites, and investigated a different state in multisite Ce compounds by measuring the fundamental properties of newly prepared polycrystalline and single-crystalline $CePtGe_2$ samples.

II. EXPERIMENTAL METHOD

Polycrystalline $CePtGe_2$ was synthesized by arc melting under a pure argon atmosphere. Because the as-grown polycrystalline samples contained impurity phases, they were annealed at 700, 750, 900, and 1000 °C. A single-phase $YrIrGe_2$-type crystal structure was confirmed after annealing at 750 °C and 900 °C via x-ray diffraction measurement; however, impurity phases remained after annealing at 700 °C, and the sample annealed at 1000 °C contained different impurities such as Ge_2Pt_3. Single-crystalline $CePtGe_2$ was grown using the flux method, with Pb and Bi as solvents. The samples

*t-nakano@eng.niigata-u.ac.jp

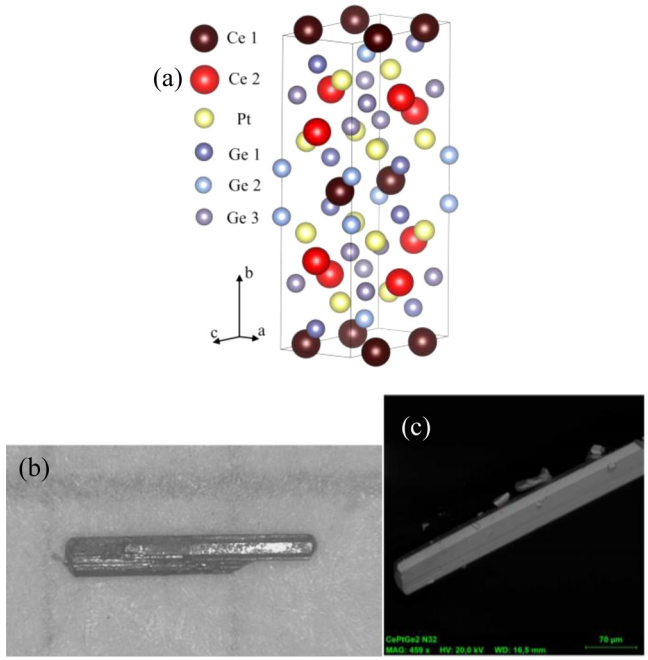

FIG. 1. (a) The crystal structure of $CePtGe_2$. (b) A single crystal of $CePtGe_2$ grown under Bi flux. (c) Scanning electron microscopy image of a single crystal of $CePtGe_2$ grown under Pb flux.

grown under Bi flux were slightly larger than those grown under Pb flux, however, Bi flux remained on the surface of samples, as shown in Fig. 1(b). From four- and three-axis x-ray measurement using a single crystal, the space group was confirmed, and the crystal axes were determined first, then the *a* axis was inferred from the shape of the sample in the measurements. In contrast, no flux remained on the samples grown under Pb flux, as shown in Fig. 1(c). Energy-dispersive x-ray spectroscopy measurements indicated a 1 : 1 : 2 (Ce/Pt/Ge) composition for each sample. Electrical resistivity was measured by the four-probe method using a ^{4}He cryostat. DC susceptibility was measured using a commercial superconducting quantum interference magnetometer (Magnetic Property Measurement System; Quantum Design, Inc.). Specific heat was measured with the Physical Properties Measurement System (Quantum Design, Inc.) using a relaxation method. The Seebeck coefficient was measured using the seesaw heating method with a standard glass Dewar [23].

III. RESULTS AND DISCUSSION

Figure 2(a) shows the resistivity of the $CePtGe_2$ polycrystalline sample annealed at 900 °C as a function of temperature. The logarithmic plot provided in the inset of Fig. 2(a) shows a Kondo-like increase in resistivity with decreasing temperature from room temperature, and the maximum resistivity was observed at approximately 50 K. Then, it decreases and shows a downward bend at 3.8 K, consistent with the antiferromagnetic/ferrimagnetic transition temperature reported in Ref. [21]. The samples annealed at 700, 750, and 1000 °C showed similar anomalies around 3.8 K, whereas the anomaly observed in the as-grown sample was broader. In contrast, no anomaly corresponding to a ferromagnetic transition temperature of ∼5.1 K (as reported in Ref. [22]) was found in all our samples.

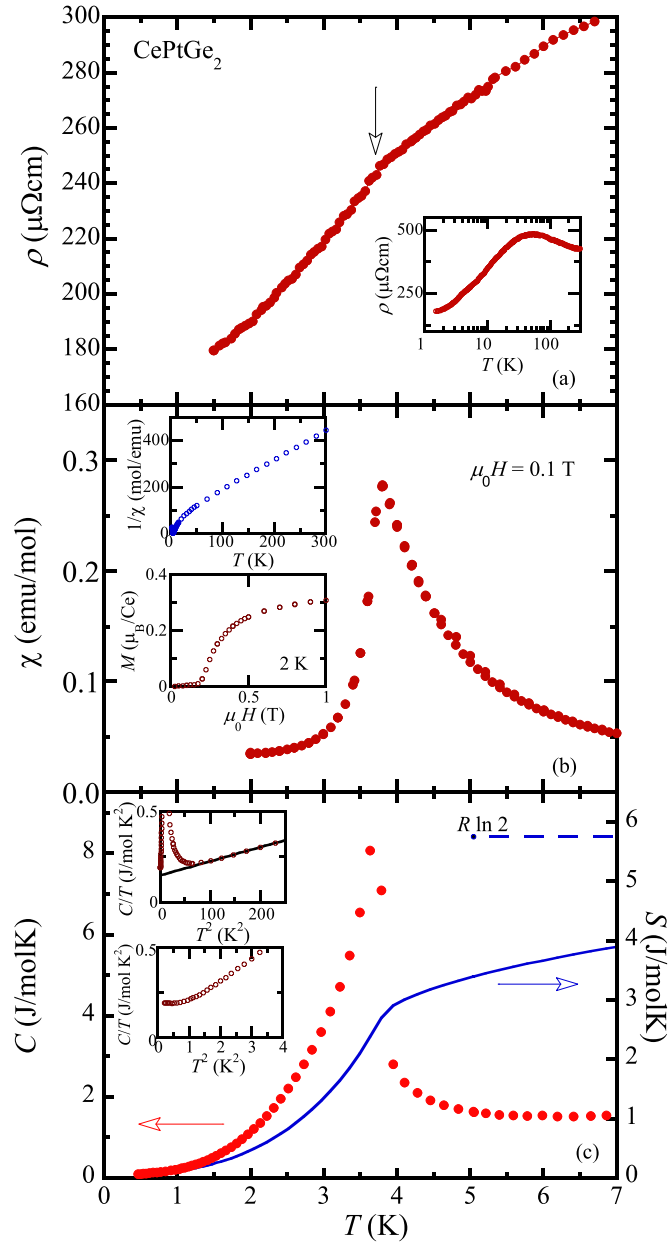

FIG. 2. (a) Resistivity of $CePtGe_2$ in the low-temperature region. The inset shows the resistivity in the entire temperature range. (b) Susceptibility of $CePtGe_2$ as a function of temperature. The insets show the inverse susceptibility and field dependence of magnetization. (c) Temperature dependence of specific heat and entropy for $CePtGe_2$. The insets show C/T versus T^2 in the entire temperature range and in the low-temperature region.

Figure 2(b) shows the temperature dependence of susceptibilityχ. The top inset of Fig. 2(b) shows the inverse susceptibility, $1/\chi$, as a function of temperature, indicating a Curie-Weiss linear dependence of $1/\chi$ down to 50 K. The Weiss temperature and effective moment were determined as −46 K and 2.51 μ_B, respectively, which are consistent with previously reported values [21], indicating

an antiferromagnetic interaction and trivalent state at both Ce sites. The susceptibility shows a clear antiferromagnetic peak at 3.8 K [Fig. 2(b)], but no ferromagnetic anomaly within the entire temperature range. The maximum value of χ ($\sim$0.3 emu/mol) observed at approximately 3.8 K is significantly larger than those reported for typical heavy-fermion Ce compounds. For example, the maximum χ values of $CeCu_6$ and $CeRu_2Si_2$ are 0.08 and 0.04 emu/mol, respectively. This indicates that the f electrons in $CePtGe_2$ are in a well-localized state. In contrast, χ is almost independent of temperature in the low-temperature region, and extrapolation of the data yields residual susceptibility $\chi(0\,\mathrm{K}) = 0.03$ emu/mol, which is on the same order of those for heavy-fermion $CeCu_6$ and $CeRu_2Si_2$. Notably, temperature independent susceptibility $c_0 = 0.0018$ emu/mol, which was estimated using the modified Curie-Weiss law $\chi = C/(T + \Theta) + \chi_0$, is one order smaller than $\chi(0$ K), where C and Θ are Curie and Weiss constant, respectively.

The lower inset of Fig. 2(b) shows the magnetic field dependence of magnetization M, indicating that M increases linearly up to a magnetic field of 0.2 T. Magnetization shows a metamagnetic increase between 0.2 and 1 T, and then it increases gradually at magnetic fields above 1 T. No hysteresis or residual magnetization was observed in our sample.

Figure 2(c) shows the temperature dependence of specific heat C, revealing a λ-type anomaly at 3.8 K corresponding to a second-order transition. The insets of Fig. 2(c) show C/T as a function of T^2. At temperatures higher than the transition temperature, C/T follows the relation $C/T = \gamma + \beta T^2$, where γ is the Sommerfeld coefficient and β is a constant related to the phonon contribution. In this study, γ and the Debye temperature (Θ_D) were evaluated as 150 mJ/mol K^2 and 215 K, respectively. However, the difficulty in evaluating γ based on data in the high-temperature region might result in an error. Nonetheless, the evaluated value of γ is clearly larger than that for a normal metal. This indicates that $CePtGe_2$ exists in the itinerant heavy-fermion state at just above the transition temperature, even though the susceptibility suggests a well-localized f-electron state. In the low-temperature region, γ is 200 mJ/molK^2, as shown in the lower inset of Fig. 2(c). Although this value is nearly twice that reported in Ref. [21], both values are larger than expected for a normal metal, indicating that the heavy-fermion state remains in the magnetically ordered state. Magnetic entropy (S_m) was evaluated after extracting the phonon contribution based on a fit of the data in the high-temperature region. Despite that the doublet ground state of the $J = 5/2$ multiplet of Ce^{3+} is predicted, S_m was the nearly half of $R\ln 2$ around the transition temperature, where R is the gas constant.

Therefore, our results are consistent with those reported by Pecharsky *et al.* [21]. This $CePtGe_2$ was found to show an antiferromagnetic/ferrimagnetic transition at 3.8 K, and no evidence of a ferromagnetic transition at approximately 5 K was observed. Furthermore, the clear antiferromagnetic anomaly in $\chi(T)$ and the lack of residual magnetization in $M(H)$ indicate that the magnetism in $CePtGe_2$ is antiferromagnetic rather than ferrimagnetic. Thus, we can conclude that $CePtGe_2$ herein is antiferromagnetic with a transition temperature $T_N = 3.8$ K. Conversely, we could not find any sign of ferromagnetism even in polycrystals and single crystals. Usually, the shape of a single crystal grown via the flux method depends on the crystal structure. However, the shape of the ferromagnetic single crystal (platelet-like shape) [22] is quite different from that of the antiferromagnetic crystal (columnar-like shape), as shown in Figs. 1(b) and 1(c), indicating different crystal structures. Even in polycrystalline samples, no ferromagnetic sign indicates that ferromagnetic character is not realized in our samples through imperfections such as dislocation, strain, and impurities. Thus, we consider that the difference between both samples results from their different local environments, such as point symmetry, the crystal electric field, molecular field, and valence; hence, both samples should be regarded as different compounds. Accordingly, crystal polymorphism and a slight change of composition or crystal structure are expected, and investigating such samples is necessary. In the following, we discuss the $CePtGe_2$ sample, which exhibits the antiferromagnetic transition at 3.8 K.

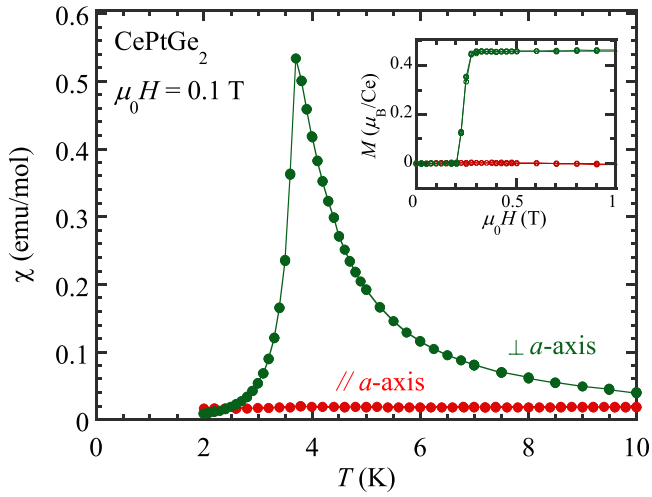

FIG. 3. Temperature dependence of χ for single-crystalline $CePtGe_2$. The inset shows the magnetic field dependence of magnetization at 2 K.

Although the above results clarify the antiferromagnetism in this $CePtGe_2$, the following contradictions remain:

(1) The value of γ below T_N seems to have the same order as above T_N, despite the ordered state of $CePtGe_2$ below T_N.

(2) The entropy at T_N is much less than $R\ln 2$ despite the doublet ground state of the $J = 5/2$ multiplet with orthorhombic symmetry.

(3) A large value of χ just above T_N lets us predict a well-localized f-electron state but the larger residual $\chi(0$ K) is also of the same order as that of typical itinerant heavy-fermion Ce compounds.

To understand these contradictions, we prepared single-crystalline $CePtGe_2$ samples and measured their fundamental properties. It should be noted that the sample mass was less than 0.1 mg, resulting in a large background effect. However, with the exception of the Seebeck coefficient, all measurements were performed using the same single-crystalline sample grown by the Pb-flux method.

Figure 3 shows the temperature dependence of χ for a single crystal of $CePtGe_2$. $\chi(T)$ perpendicular to the a axis

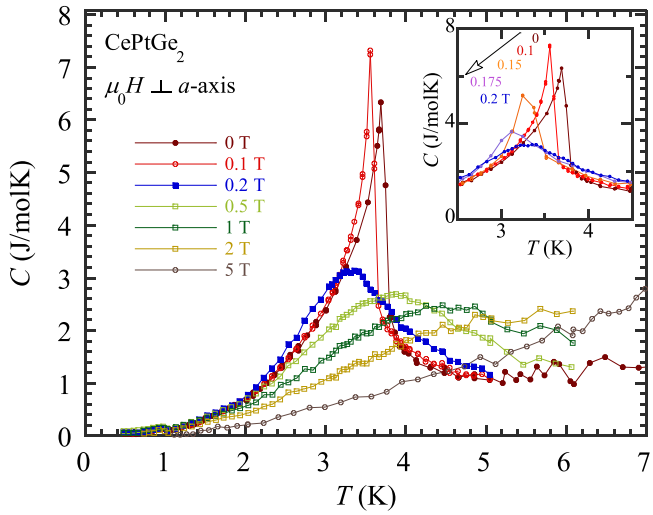

FIG. 4. Temperature dependence of specific heat for a single crystal of $CePtGe_2$. The inset shows the expansion around T_N.

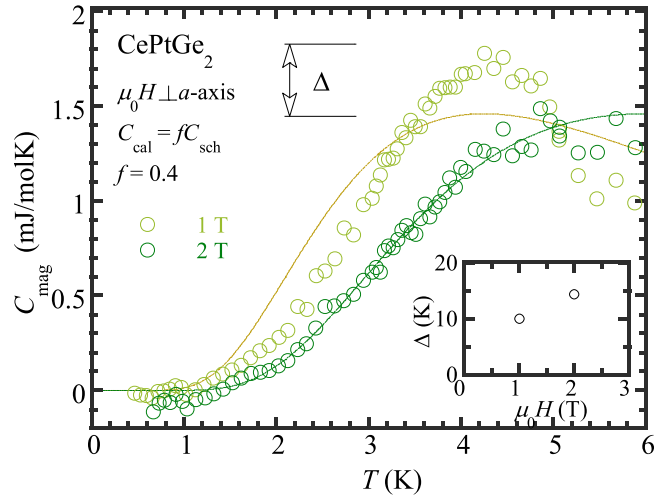

FIG. 5. Magnetic contribution to the specific heat for a $CePtGe_2$ single crystal.

shows a strong temperature dependence with an antiferromagnetic peak at $T_N = 3.8$ K. In contrast, $\chi(T)$ parallel to the a axis shows a weak temperature dependence. This strong anisotropic behavior is indicative of a strong crystal electric field. The maximum value of χ ($\sim$0.5 emu/mol) at T_N is on the same order as that for polycrystalline $CePtGe_2$, indicating well-localized f electrons. With increasing magnetic field, T_N decreases, i.e., the antiferromagnetic peak shifts to lower temperatures and is not observed in magnetic fields above 0.3 T (not shown) perpendicular to the a axis. The inset of Fig. 3 shows the magnetic field dependence of magnetization for each axis. For the a axis, M is almost independent of H. In contrast, M perpendicular to the a axis shows a sudden increase around $\mu_0 H_c = 0.2$ T, but no clear hysteresis around H_c. Above H_c, M shows a plateau. These behaviors are different from those observed in normal antiferromagnetic compounds. Sudden increases and plateau behavior are often observed in chiral magnetism. However, the lack of helical symmetry in the crystal structure of $CePtGe_2$ rules out a typical chiral magnetic structure. On the other hand, Ising antiferromagnets due to the first order transition to the polarized paramagnetic state also show such behaviors [24], although no hysteresis is present in magnetization curve at 2 K for $CePtGe_2$. Thus the magnetization measurement at lower temperature would reveal this issue.

Figure 4 shows the temperature dependence of specific heat at the magnetic field perpendicular to the a-axis. C shows a clear λ-type peak at T_N. This peak shifts toward lower temperature with increasing magnetic field and disappears completely at a magnetic field above 0.2 T. This magnetic field agrees with $\mu_0 H_c$ at which the M exhibits a sudden increase as shown in the inset of Fig. 3. Above 0.5 T, a Schottky-like or a first-order-like symmetric anomaly emerges, and it shifts toward high temperatures and broadens with increasing magnetic field. These obtained results suggest the following simple scenario. $CePtGe_2$ has two crystallographically nonequivalent Ce sites, and each Ce ion has a different local environment. As a result, the f electrons at each site might have different characteristics. Assuming that each f electron has different characteristics, one site would have the heavy itinerant character and another would have localized character. Indeed, as mentioned above, magnetic entropy is nearly half Rln 2 at T_N. To confirm this assumption, we roughly analyzed the Schottky anomaly in specific heat data. The Schottky specific heat $C_{\rm cal} = fC_{\rm sch}$ is shown in Fig. 5, where f is a fraction factor and $C_{\rm sch}$ is calculated assuming the singlet-singlet state split from the doublet ground state, on the basis of experimental $C_{\rm mag}$ in $\mu_0 H = 1$ T and 2 T. Herein, $C_{\rm mag}$ was obtained by extracting the phonon contribution. The values of $fC_{\rm ch}$ are in rough agreement with the experimental data for $f = 0.4$. This f value, is nearly 1/2, is consistent with the above suggestion. The energy gap Δ between the ground and excited states increases with increasing magnetic field as shown in the inset of Fig. 5.

In addition, the temperature dependences of the Seebeck coefficient for single-crystalline and polycrystalline (inset) $CePtGe_2$ are shown in Fig. 6. Both Seebeck coefficients are maximized at approximately 120 K and exhibit shoulders

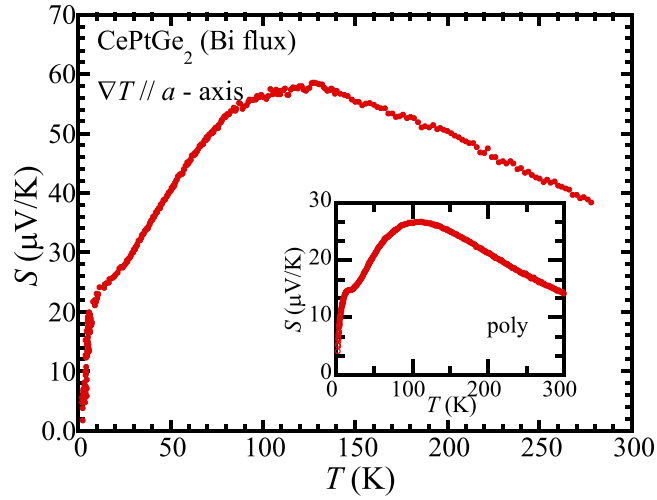

FIG. 6. Temperature dependence of the Seebeck coefficient for single-crystalline and polycrystalline (inset) $CePtGe_2$.

at approximately 10 K, indicating the Kondo effect affected by the crystal electric field. Usually, Ce compounds with an antiferromagnetic order typically show negative Seebeck coefficients in the low-temperature region. However, those of $CePtGe_2$ is positive at temperatures as low as 1.5 K, indicating an itinerant state with relatively strong hybridization, similar to that observed in the high-pressure region for $CeCu_2Si_2$ [25]. Thus, these results are consistent with the above discussion.

Finally, we will discuss the significant increase and plateau in magnetization observed with increasing H. In the typical antiferromagnetism, the magnetization curve shows a gradual increase from the antiferromagnetic to the paramagnetic state via canting in the magnetic moment. However, the large M value on the plateau in the magnetization curve of $CePtGe_2$ indicates that a polarized paramagnetic state was realized suddenly under the magnetic field of only 0.2 T. This metamagnetic transition by the magnetic field may be assisted by the interaction between the localized and the itinerant heavy f electrons. Measurements of specific heat and magnetization using single crystals of a larger mass along with applying microscopic methods, such as photoelectron, neutron, NMR, and μSR spectroscopies, are necessary to elucidate the character of f electrons in $CePtGe_2$. A new situation, i.e., the coexistence of ordered localized moments and heavy itinerant electrons, provides the opportunity for a different type of quantum criticality and fluctuations. Tuning a particular system applying pressure and chemical substitution, may contribute to the discovery of different phenomena.

IV. SUMMARY

In summary, we have prepared polycrystalline and single-crystalline samples of $CePtGe_2$ and measured their magnetization, specific heat, resistivity, and Seebeck coefficient to clarify previous conflicting reports of antiferromagnetic and ferromagnetic ground states below 3.8 and 5.1 K, respectively. We observed a bend in resistivity, a peak in susceptibility, and a λ-type anomaly in specific heat at 3.8 K, and a metamagnetic transition at low temperatures. These results confirm antiferromagnetism with $T_N = 3.8$ K whereas no evidence of ferromagnetic order was found in the studied temperature range, indicating possible crystal polymorphism with ferromagnetic character. The large susceptibility just above T_N and the Schottky anomaly in specific heat indicate a well-localized f-electron state, whereas the large residual γ and $\chi(0)$ indicate an itinerant heavy f-electron state. Thus, we propose the coexistence of localized and heavy itinerant characters in the antiferromagnetic $CePtGe_2$; that is, the f electrons at one Ce site show localized characters, whereas those at the other Ce site show itinerant characters. A new situation, i.e., the coexistence of ordered localized moments and heavy itinerant electrons, might represent a different state in multisite Ce compounds although the origins of the collapse in the antiferromagnetic order under weak magnetic fields and the plateau above the critical magnetic field remain unclear.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grants No. JP15K05162, No. JP24740226, and No. JP15KK0156. The single-crystal growth and characterization together with majority of measurements on single crystals were accomplished in MGML (http://mgml.eu), which is supported within the program of Czech Research Infrastructures (Project No. LM2018096). The authors are indebted to Dr. R. Colman for critical reading and correcting the manuscript.

[1] B. Barbara, J. X. Boucherle, J. L. Buevoz, M. F. Rossignol, and J. Schweizer, Solid State Commun. **24**, 481 (1977).
[2] T. Nakano and I. Terasaki, Phys. Rev. B **73**, 195106 (2006).
[3] H. Yamagami and A. Hasegawa, Physica B **186–188**, 182 (1993).
[4] A. Severing, E. Gratz, B. D. Rainford, and K. Yoshimura, Physica B **163**, 409 (1990).
[5] D. W. Pohl, Phys. Rev. B **15**, 3855 (1977).
[6] A. Schenck, F. N. Gygax, D. Andreica, and Y. Onuki, J. Phys.: Condens. Matter **15**, 8599 (2003).
[7] K. Hanzawa and T. Kasuya, J. Phys. Soc. Jpn. **53**, 1809 (1984).
[8] A. Sakai and S. Nakatsuji, J Korean Phys. Soc. **63**, 398 (2013).
[9] N. D. Mathur, F. M. Grosche, S. R. Julian, I. R. Walker, D. M. Freye, R. K. W. Haselwimmer, and G. G. Lonzarich, Nature (London) **394**, 39 (1998).
[10] M. P. Allan, F. Massee, D. K. Morr, J. Van Dyke, A. W. Rost, A. P. Mackenzie, C. Petrovic, and J. C. Davis, Nat. Phys. **9**, 468 (2013).
[11] M. Tsujimoto, Y. Matsumoto, T. Tomita, A. Sakai, and S. Nakatsuji, Phys. Rev. Lett. **113**, 267001 (2014).
[12] N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S. W. Cheong, Nature (London) **429**, 392 (2004).
[13] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[14] I. Terasaki, Y. Sasago, and K. Uchinokura, Phys. Rev. B **56**, R12685(R) (1997).
[15] I. Terasaki, M. Iwakawa, T. Nakano, A. Tsukuda, and W. Kobayashi, Dalton Trans. **39**, 1005 (2010).
[16] S. Ishiwata, T. Nakano, I. Terasaki, H. Nakao, Y. Murakami, Y. Uwatoko, and M. Takano, Phys. Rev. B **83**, 020401(R) (2011).
[17] F. G. Aliev, N. B. Brandt, V. V. Moshchalkov, and S. M. Chudinov, Solid State Commun. **45**, 215 (1983).
[18] F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz, and H. Schäfer, Phys. Rev. Lett. **43**, 1892 (1979).
[19] V. Babizhetskyy, O. Isnard, and K. Hiebl, Solid State Commun. **142**, 80 (2007).
[20] A. V. Gribanov, Y. D. Seropegin, and O. I. Bodak, J. Alloys Comp. **204**, L9 (1994).
[21] V. K. Pecharsky, L. L. Miller, K. A. Gschneidner, Jr., and D. C. Johnston, Phys. Rev. B **51**, 954 (1995).

[22] S. Kirita, A. Thamizhavel, T. Takeuchi, K. Tabata, T. C. Kobayashi, A. Galatanu, E. Yamamoto, R. Settai, S. Ramakrishnan, and Y. Onuki, J. Phys. Soc. Jpn. **72**, 2338 (2003).

[23] M. Hedo, D. Nakamura, Y. Takaesu, T. Fujiwara, K. Uchima, K. Yagasaki, and T. Nakama, J. Phys.: Conf. Series **215**, 012186 (2010).

[24] J. Valenta, F. Honda, M. Vališka, P. Opletal, J. Kaštil, M. Míšek, M. Diviš, L. Sandratskii, J. Prchal, and V. Sechovský, Phys. Rev. B **97**, 144423 (2018).

[25] G. Seyfarth, A. S. Rüetschi, K. Sengupta, A. Georges, D. Jaccard, S. Watanabe, and K. Miyake, Phys. Rev. B **85**, 205105 (2012).