Magnetic field–Temperature Phase Diagram of CeCoSi Constructed by Specific Heat, Magnetoresistivity, and Magnetization Measurements for a Single Crystal

Hiroyuki Hidaka1,* Shun Yanagiya1, Eiikai Hayasaka1, Yuma Kaneko1, Tatsuya Yanagisawa1, Hiroshi Tanida2, and Hiroshi Amitsuka1

1Graduate School of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan
2Liberal Arts and Sciences, Toyama Prefectural University, Toyama 939-0398, Japan

A Ce-based metallic compound CeCoSi with a tetragonal structure exhibits successive phase transitions: the one whose order parameter is unidentified at \( T_0 \sim 12 \) K and the antiferromagnetic one at \( T_N = 9.4 \) K. [H. Tanida et al., J. Phys. Soc. Jpn. 88, 054716 (2019)] We performed specific heat, magnetoresistivity (MR), and magnetization measurements for a single crystal CeCoSi at low temperatures in magnetic fields \( B \) of up to 14 T and constructed detailed magnetic field–temperature phase diagrams for both \( B \parallel [100] \) and \( [001] \). The longitudinal MR measured for \( B \parallel [100] \) shows a sign change from negative to positive across \( T_0 \sim 13 \) K updated in the present sample, indicating a clear change in an electronic state. In addition, the constructed magnetic phase diagrams for both the field directions have a \( B \)-induced region in each ordered state. The presence of the newly found regions would be attributed to a change in the symmetry of the order parameter or domain alignment by applying \( B \).

An ordered state in solids has been understood by revealing changes in symmetry of the relevant system, such as point-group, translational, and time-reversal symmetries, accompanied with the phase transition. However, there is an enigmatic ordering whose order parameter (OP) is unidentified, called a “hidden order”, in several materials, such as URu$_2$Si$_2$\(^{1,2}\) and studies to reveal their OPs are being vigorously carried out. In recent years, the presence of an ordering of multipole degrees of freedom has been established both experimentally and theoretically through attempts to elucidate the hidden order. Here, the multipole is defined as anisotropic distribution of electric or magnetic charge.\(^{3,4}\) The 4f electron system CeCoSi has also been recently reported to be a new member of the family showing the hidden order.\(^{5,6}\) The hidden order in CeCoSi has attracted much attention because of a lack of the local space-inversion symmetry at Ce sites,\(^{7,8}\) where an odd-parity multipole in addition to an even-parity one is expected to play a some role in the phase transitions and the electronic state.\(^{9}\)

CeCoSi crystallizes in the tetragonal CeFeSi-type structure with the space group \( P4/\text{mmm} \) (No. 129, \( D_{4h}^4 \)),\(^{7,9}\) where the space-inversion symmetry at the Ce sites is locally broken. This compound exhibits two successive phase transitions: an antiferromagnetic (AFM) ordering at \( T_N = 9.4 \) K and the hidden ordering at \( T_0 \sim 12 \) K.\(^{5,6}\) Here, the paramagnetic (PM) state above \( T_0 \), an intermediate state for \( T_N < T < T_0 \), and the AFM state below \( T_N \) are named phase I, II, and III, respectively. Recent neutron diffraction measurements suggested that the Ce moments with the size of 0.37(6) \( \mu_B/\text{Ce} \) are aligned along the [100] direction with a \( q = 0 \) structure in the AFM state.\(^{10}\) On the other hand, the possibility of an antiferroquadrupole (AFQ) ordering of Ce 4f electron has been suggested as candidate for the hidden order below \( T_0 \) from the fact that \( T_0 \) increases with increasing magnetic field \( B \) at least up to 7 T.\(^{5,6}\) The Co-NQR measurements for a single crystalline CeCoSi revealed that the 4-fold symmetry and the time-reversal symmetry are preserved at the Co sites below \( T_0 \), suggesting the AFQ or higher electric multipole ordering.\(^{11}\) However, a Kramers doublet crystalline-electric-field (CEF) ground state (GS) without the quadrupole degrees of freedom and CEF excited states located at an order of 100 K seems to be incompatible with the AFQ ordering at \( T_0 \) of 12 K\(^{6,10,12}\) and an obscure anomaly in bulk properties at \( T_N \)\(^{11}\) is different from that observed in conventional AFQ ordering compounds.\(^{13-16}\) Thus, it should be essential to reveal a detailed magnetic field–temperature \((B-T)\) phase diagram of CeCoSi up to higher magnetic fields including its anisotropy with respect to magnetic field direction, because the magnetic phase diagram will give us fundamental and important information about the ordered states. In the present study, we have performed specific heat \( C \), electrical resistivity \( \rho \), and magnetization \( M \) measurements for a single crystalline CeCoSi in high magnetic fields up to 14 T and constructed the detailed \( B-T \) phase diagrams for \( B \) applied parallel to the tetragonal [100] and [001] axes.

A single crystal of CeCoSi was prepared by a Ce/Co eutectic flux method as described in the previous paper.\(^{9}\) The dimensions of the thin plate-like sample are \( 2.0 \times 1.0 \times 0.2 \) mm\(^3\) for the tetragonal [100]–[010]–[001] axes. The \( C \) measurements were performed by a thermal-relaxation method in the temperature range \( 2-300 \) K at magnetic fields of \( B = 0 \) and 6 T with a physical property measurement system (PPMS; Quantum Design). The \( B \) was applied along [100]. The \( \rho \) measurements were performed by a conventional four probe method in the temperature range of \( 2-300 \) K and in the magnetic field range of from –14 to 14T with the PPMS. We measured the magnetoresistivity (MR) in two different configurations: a longitudinal MR with the electrical current \( J \parallel [100] \) and \( B \parallel [100] \), and a transverse MR with \( J \parallel [100] \) and \( B \parallel [001] \). The DC \( M \) measurements were performed in the temperature range of \( 2-300 \) K and in the magnetic field range of 0–7 T with a magnetic property measurement system (PPMS; Quantum Design). The \( B \) were applied along the [100] and [001] directions. All the measurements in the present study were carried out using the same single sample.
First, we show the $B - T$ phase diagrams of CeCoSi constructed from the present $C$, $\rho$, and $M$ measurements for $B \parallel [100]$ and $[001]$ as Figs. 1(a) and 1(b), respectively. The details of each measurement will be described later. The main revealed feature is that these phase diagrams have $B$-induced regions in the ordered states for both the field directions. Here, we refer to these $B$-induced regions as $\Pi_a$ and $\Pi'_a$ for $B \parallel [100]$, and $\Pi'_{c}$ for $B \parallel [001]$.

Figure 2 shows the temperature dependence of $C_{Jf}$ in CeCoSi at $B = 0$ and $6 \, T$ for $B \parallel [100]$. Here, $C_{Jf}$ is the contribution of $J_f$ electrons to the specific heat, which was estimated by subtracting $C$ of LaCoSi at zero field from $C$ of CeCoSi. The obtained features of $C_{Jf}(T)$, which are a $\lambda$-type anomaly at $T_N$, a small jump at $T_0$, and a CEF Schottky anomaly around $40 \, K$, are in good agreements with those reported previously. The value of $T_0$ at zero field is estimated to be $\sim 13 \, K$ in the present sample, which is slightly higher than that of $12 \, K$ reported previously. The blue curve represents the calculated CEF Schottky curve based on the previously suggested CEF level scheme. Application of $B$ of $6 \, T$ hardly affects $C_{Jf}(T)$ except for a slight decrease of $T_N$ and an increase of $T_0$. The magnitude of the jump at $T_0$ also hardly changes despite the increase in the transition temperature from $13$ to $14 \, K$, as shown in the inset of Fig. 2. The obtained $T_0$ and $T_N$ are plotted in the $B$-$T$ phase diagram [Fig. 1(a)]. Note that the present $C$ measurement at $6 \, T$ does not show any clear anomaly at $B_N$, which separates the $\Pi$ and $\Pi'_a$ regions.

Figures 3(a) and 3(b) show the temperature dependence of the electrical resistivity $\rho(T)$ below $30 \, K$ at magnetic fields up to $14 \, T$ for CeCoSi. The electric current was applied along the $[100]$ direction, and the magnetic fields were applied along the $[100]$ and $[001]$ directions in Figs. 3(a) and 3(b), respectively. The $\rho(T)$ data at zero field shows no clear anomaly at $T_0$, although $\rho$ seems to decrease slightly below $T_0$ determined from $C(T)$. On the other hand, $\rho(T)$ shows a clear kink anomaly at $T_N$. These results at zero field are consistent with the previous report. In addition, small residual resistivity of $\sim 3 \, \mu\Omega\text{cm}$ guarantees the high quality of the present sample.

When the magnetic field is applied along the $[100]$ direction, $\rho(T)$ seems to be hardly affected by $B$, as can be seen in Fig. 3(a). However, in the longitudinal MR measurements for $J$ and $B \parallel [100]$, $\rho(B)$ shows a clear kink when crossing the phase boundary between the phases I and II. Figure 4(a) shows the longitudinal MR of CeCoSi for $J$ and $B \parallel [100]$ at several temperatures between $10$ and $20 \, K$ in the field range from $-14$ to $+14 \, T$. Here, the data are shifted vertically for clarity. At $20 \, K$ corresponding to the PM state, $\rho(B)$ shows a monotonic decrease with increasing $B$, which should be due to suppression of the magnetic scattering between the $4f$ and conduction electrons. Below $17 \, K$, one can see a kink anomaly at a high field of $\sim 13 \, T$. The corresponding field of the kink anomaly is defined as $B_0$, since the $B_0$ decreases with decreasing temperature down to $14 \, K$ and it appears to merge the $T_0(B)$ curve in the $B$-$T$ phase diagram. It is characteristic that the sign of MR changes from negative to positive below $T_0 \sim 13 \, K$. This sign change in MR indicates a change in the electronic state of CeCoSi accompanied by the $T_0$ transition, and is the first obvious observation of the $T_0$ transition in the...
electrical transport measurement. In addition, we found another anomaly above ~ 5 T below $T_0$, which increases with decreasing temperature. This result suggests the presence of a high-field region, named as II$''$, above the region II. Here, the corresponding field of the newly found anomaly below $T_0$ is defined as $B_x$. The results of the longitudinal MR for $B \parallel [100]$ in the AFM state are shown in Fig. 4(b). These $\rho(B)$ curves show the positive MR, although the curve changes gradually from downward to upward convex with decreasing temperature. The anomaly observed at 9 K corresponds the transition of CeCoSi for $J \parallel [100]$. From these results, we propose the presence of the region II$''$, and any anomaly corresponding to $B_x$ was not observed in the AFM state.

On the other hand, the $\rho(T)$ curves show the monotonous positive MR below ~ 20 K when the magnetic field is applied along the [001] direction, as shown in the Fig. 3(b). The decrease in $T_N$ is greater than that for $B \parallel [100]$. The transverse MR with $J \parallel [100]$ and $B \parallel [001]$ exhibits quadratic-like behavior below 20 K, and no anomalies corresponding to $B_0$ and $B_x$ are observed. The details of the obtained transverse MR are indicated in the Supplemental Materials (SM).18

Figures 5(a) and 5(b) show the magnetization process $M(B)$ of CeCoSi for $B \parallel [100]$ and [001] up to 7 T, respectively, measured at temperatures between 2 and 30 K. The respective derivative $dM/dB$ for $B \parallel [100]$ and [001] are also shown in Figs. 5(c) and 5(d), respectively. The indicated data are shifted vertically for clarity in these figures. The steep decrease in $dM/dB$ near zero field, observed in all the derivative data, may be due to magnetic impurity. We also confirmed that the temperature dependence of the magnetic susceptibility for both the field directions in the present sample are in good agreements with that reported previously, indicated in the SM.5,18 and the obtained transition temperatures are summarized in the $B$–$T$ phase diagram (Figs. 1).

The $M(B)$ curves for $B \parallel [100]$ seem to be simple linear behavior at all the measured temperatures; however, slight deviation from the linear behavior can be seen at low temperatures, as shown in the derivative data [Fig. 5(c)]. The $dM/dB$ curves above 16 K are almost constant, whereas it at 14 K starts to increase around $B_0$ determined from the present MR measurement. This behavior is consistent with the larger magnetic susceptibility in the ordered state below $T_0$ than that in the PM state. Below $T_0$ ~ 13 K, $dM/dB$ shows a broad maximum at the magnetic field corresponding to $B_x$. This result also suggests the presence of the region II$''$. The absence of the maximum in data at 10 K is due to that $B_x$ is present above 7 T, which is above the measurement field range. In addition, the $dM/dB$ curves below $T_N$ show another maximum at $B_{M'}$ accompanied by hysteresis below ~ 2 T, suggesting the presence of a $B$-induced region, named III$'''$, even in the AFM ordered state.

A similar maximum in the $dM/dB$ curve below $T_0$ is observed even in the measurements for $B \parallel [001]$, as shown in Fig. 5(d). In this case, the field showing the maximum, named $B_{M'}$, appears to increases continuously as the temperature decreases across $T_N$, although the maximum changes to the one accompanied with the hysteresis in the AFM state as well as the results for $B \parallel [100]$. From these results, we propose the presence of region II$'$ and III$'$ above $B_{M'}$ in the phase diagram for $B \parallel [001]$. We now discuss the characteristics of the $B$–$T$ phase diagrams revealed from the present study. First, $T_0$ increases and $T_N$ decreases with increasing $B$ up to 14 T for both the field directions, where the $B$ effects on these ordering temperatures are larger for [001] than for [100]. Note that there is no direct experimental evidence to determine $T_0$ for [001] above 7 T. However, the phase II for $B \parallel [001]$ may be induced by lower $B$ than that for [100] at a fixed temperature above $T_0$, since the $dM/dB$ for [001] at 14 K starts to increase from the lower $B$ than that observed for [100] [see Figs. 5(c) and 5(d)]. This anisotropic $B$ dependence of the ordering temperatures should
be attributed to the symmetry of each order parameter. Such an anisotropic increase in $T_N$ by the application of $B$ is similar to a typical characteristic of the electric quadrupolar ordering, regardless of whether it is a ferroquadrupolar or AFQ ordering.\(^{13-16,19,20}\) It has been revealed that the critical field of the AFM state has been determined to be $\sim 20$ T by the high-field $M$ measurements.\(^{6}\) Although it has not been clarified whether $T_N$ tends towards absolute zero or disappears under higher magnetic fields at present, it is an important issue in order to elucidate the ordered state of the phase II in CeCoSi. Experiments under higher magnetic field are required.

Second, it is suggested that each ordered state of CeCoSi has the $B$-induced region for both $B \parallel [100]$ and $[001]$, which is associated with a change in the symmetry of OP or alignment of domains by the application of $B$. It is commented that very recent X-ray diffraction measurements for a single crystalline CeCoSi also reveal the presence of the $B$-induced regions.\(^{21}\) In addition, the change in the OP from hexadecapole or $O_{2g}$-type AFQ to $O_{4g}$-type AFQ has been pointed out in the Co-NMR measurements of CeCoSi at $B = 1$ T for $B \parallel [100]$ by Manago et al.\(^{11}\) Assuming the quadrupole ordering below $T_N$ in the present compound, the stable state under high magnetic field is considered to be determined by the energy gain due to the induced moments, such as magnetic dipole and octupole moments.\(^{22}\) This possible change in the stable state would result in the suppression of the magnetic scattering in the MR and the small anomaly in the magnetization process. Similar anomaly in the MR accompanied with emergence of the $B$-induced phase has also been reported in an AFQ ordering compound $PrPb_2$,\(^{23}\) where the AFQ OP has been suggested to change from $O_2^\parallel$ to $O_2^\perp$ by applying $B$ along the cubic $[100]$.\(^{24}\)

In the AFM state in CeCoSi, the $III_{a}$ region for $B \parallel [100]$ seems to be independent of the presence of the $II_{a}$ region, while the $III_{c}$ region for $B \parallel [001]$ might relate with the $II_{c}$ region. Furthermore, the presence of the hysteresis at $B_{H_0}^M$ and $B_{H_0}^Q$ suggests the first-order phase transition, whose origin may be a change in the magnetic structure. The magnetic structure in the AFM state has been proposed to be a simple collinear one with the magnetic moments pointing along the $[100]$ direction from the previous neutron powder diffraction measurements.\(^{10}\) However, considering the small anisotropy of the magnetic susceptibility,\(^{6}\) the Co-NQR spectrum below $T_N$,\(^{11}\) and the complex magnetic phase diagram obtained in this study, the AFM magnetic structure may not be so simple one proposed by Nikitin et al. In this case, the direction of the magnetic moments could be changed by the application of small $B$. Furthermore, if the antiferro-type ordering at the Ce on-sites with $q = 0$ occurs at $T_N$, the space-inversion symmetry at the midpoint between the Ce ions is broken, resulting in the Dzyaloshinskii–Moriya (DM) interaction can be active. The DM interaction will induce a tilting of the magnetic moments in the AFM state.

Finally, the $B-T$ phase diagrams constructed in the present study could be explained by the successive phase transitions of the electric quadrupole and the magnetic dipole orderings; however, the OP in the phase II has not been settled yet, including the antiferro- or ferro-type. Most compounds showing the quadrupole ordering of $4f$ electron have the quadrupole degrees of freedom within their CEF GS, such as a $I_8$ quartet for Ce$^{3+}$ ion and a non-Kramers $\Gamma_3$ doublet for Pr$^{3+}$ ion.\(^{15,25,26}\) On the other hand, since CeCoSi has the Kramers doublet CEF GS without the quadrupole degrees of freedom within the localized $4f$-electron model ($J = 5/2$), the quadrupole moment can be induced only between the GS and the excited state located at $\sim 100$ K.\(^{6,10}\) This CEF splitting seems to be too large to drive the quadrupole ordering of the local $4f$ electron at $T_N$ of 13 K. The obscure anomaly at $T_N$ in the bulk properties of CeCoSi, such as $C(T), M(T)$ and $\rho(T)$, is also a different feature from that found in the typical compounds showing the quadrupole ordering of the localized $4f$ electron.\(^{14,16,15,24,27}\) In particular, the jump at $T_N$ in $C(T)/T$ of CeCoSi is considerably small, whereas the released entropy at $T_N$ is large ($\sim 0.8$ Rln2), suggesting the magnetic ordering of the $4f$ electron. It is noteworthy that the magnitude of the jump at $T_0$ hardly changes even at high magnetic field of 6 T. This robustness is contrast with that in other AFQ compounds, where the jump in $C(T)/T$ becomes larger as the ordered state stabilizes.\(^{14,16}\)

A higher-rank multipole than the quadrupole, which preserves the time-reversal symmetry,\(^{11}\) such as an electric hexadecapole, could also be a possible OP of the phase II of CeCoSi assuming the quasi- quartet CEF GS. Furthermore, an odd-parity multipole due to the lack of the local space-inversion symmetry at the Ce site might also play some role in this enigmatic ordering at $T_0$.\(^{6,8}\) To clarify the ordered state in each region including the high-field one, further studies, such as lattice distortion and a $B-T$ phase diagram under higher $B$ and high pressure, are needed and now in progress.

In summary, we performed the $C, \rho$, and $M$ measurements in a single-crystalline CeCoSi under magnetic field up to 14 T for $B$ parallel to the tetragonal $[100]$ and $[001]$ axes. The small jump at $T_0$ in $C(T)/T$ hardly changes by applying $B$ of 6 T in spite of an increase in $T_0$. In the MR measurements for $B \parallel [100]$, we found the sign change in MR from negative to positive across $T_0$ and new anomaly suggesting the presence of a $B$-induced region in both the ordered states. Furthermore, the $M(B)$ curves also exhibit small anomalies suggesting the $B$-induced regions not only for $B \parallel [100]$ but also [001]. These results were summarized as a $B-T$ phase diagrams for both the field directions. The presence of the $B$-induced regions may be a consequence of a change in the symmetry of the OP or domain alignment by the application of $B$, which could be a clue to unraveling the mystery of the $T_N$ transition.

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1. Supplemental Material: Transverse magnetoresistivity for B || [001]

Figure S1 shows the transverse magnetoresistivity (MR) for the electric current J || [100] and the magnetic field B || [001] below 20 K in CeCoSi. The raw data are asymmetric with respect to B due to a mixed Hall effect component that is approximately proportional to B. Here, we display the data after the Hall effect component were removed in this figure. All the transverse MR curves exhibit quadratic-like behavior below 20 K, and no anomalies corresponding to $B_0$, $B_s$, and $B_N$ are observed.

2. Supplemental Material: Magnetic susceptibility

Figures S2(a) and S2(b) show the temperature dependence of the magnetic susceptibility $\chi(T) = [M(T)/B]_0$ below 20 K in CeCoSi for $B$ || [100] and [001], respectively, at several Bs up to 7 T. A small kink anomaly at $T_0$ can be observed in these $\chi(T)$ data except for the data below 1 T for $B$ || [100]. On the other hand, a clear anomaly at $T_N$ are also observed. $T_0$ increases and $T_N$ decreases with increasing B for both the field directions. These obtained features are consistent with the results reported in the previous study. It should be commented that the anomaly observed at $T_N$ changes from the kink to a dip above 5 T for $B$ || [100], which might indicate a change in the magnetic structure in the high B region.

Fig. S1. (Color online) Transverse magnetoresistivity in CeCoSi at several temperatures in the range below 20 K. J was applied along the [100] direction, while B was [001]. The data are shifted vertically for clarity.

Fig. S2. (Color online) Temperature dependence of magnetic susceptibility $\chi(T) = [M(T)/B]_0$ in CeCoSi for $B$ || (a) [100] and (b) [001] below 20 K at several magnetic fields up to 7 T. The data are shifted vertically for clarity.