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Magnetic Field–Temperature Phase Diagram of CeCoSi Constructed on the Basis of Specific Heat, Magnetoresistivity, and Magnetization Measurements: Single Crystal Study

Hiroyuki Hidaka^{1*}, Shun Yanagiya¹, Eikai 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

The Ce-based metallic compound CeCoSi with a tetragonal structure exhibits successive phase transitions: a hidden ordering, whose order parameter is unidentified, at $T_0 \sim 12$ K and an antiferromagnetic ordering 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 (M) measurements for single crystals of 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 $[001]$. In the longitudinal MR measurements for $B \parallel [100]$, the sign of MR changes from negative in a paramagnetic state to positive in the hidden ordered state, which suggests a change in electronic state across T_0 . In addition, the longitudinal MR and magnetization processes for $B \parallel [100]$ show anomalies upon the application of B in both ordered states, suggesting the presence of B -induced regions. Similar B -induced regions may exist in the magnetic phase diagram for $B \parallel [001]$. The emergence of B -induced regions may be attributed to a change in the symmetry of the order parameter or domain alignment on applying B .

1. Introduction

An ordered state in solids has been clarified by revealing changes in the symmetries of the relevant system, such as point-group, translational, and time-reversal symmetries, accompanying the phase transition. However, there is an enigmatic ordering whose order parameter (OP) is unidentified, called a “hidden order (HO)”, in several materials, such as URu₂Si₂,^{1,2)} and studies to reveal its OP are being intensively 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 HO. Here, the multipole is characterized by the anisotropic distribution of electric or magnetic charge.^{3,4)} The $4f$ electron system CeCoSi has also recently been reported to show the HO.^{5,6)} The HO in CeCoSi has attracted considerable attention because of lack of local space-inversion symmetry at Ce sites,⁷⁾ where an odd-parity multipole, in addition to an even-parity one, is expected to play a particular role.⁸⁾

CeCoSi crystallizes in the tetragonal CeFeSi-type structure with the space group $P4/nmm$ (No. 129, D_{4h}^7),⁹⁾ where the space-inversion symmetry at Ce sites is locally broken. This compound exhibits two successive phase transitions: an antiferromagnetic (AFM) ordering at $T_N = 9.4$ K and the HO at $T_0 \sim 12$ K.^{5,6,9)} Recent neutron diffraction measurements suggested that Ce moments with a 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 $4f$ electrons has been suggested as a candidate for the HO below T_0 from the fact that T_0 increases with the magnetic field B , at least up to 7 T.^{5,6)} The Co nuclear quadrupole resonance (NQR) measurements for a single-crystalline CeCoSi revealed that the 4-fold and time-reversal symmetries are preserved at Co sites below T_0 , suggesting the AFQ or higher electric multipole order-

ing.¹¹⁾ However, a Kramers doublet crystalline-electric-field (CEF) ground state (GS) without the quadrupole degrees of freedom and CEF excited states located at approximately 100 K seem to be incompatible with the AFQ ordering at T_0 of 12 K.^{6,10,12)} Furthermore, an obscure anomaly in bulk properties at T_0 ⁶⁾ is different from that observed in conventional AFQ ordering compounds.^{13–16)} In addition, very recent X-ray diffraction (XRD) measurements on a single-crystalline CeCoSi revealed that a triclinic lattice distortion occurs below T_0 ,¹⁷⁾ and its relationship with the results of the NQR measurements must be clarified. Thus, it is essential to obtain a detailed magnetic field–temperature (B – T) phase diagram of CeCoSi up to high magnetic fields, including its anisotropy with respect to the B direction, because the magnetic phase diagram will provide fundamental and important information about the ordered states.

In the present study, we have performed specific heat C , electrical resistivity ρ , and magnetization M measurements for single crystals of CeCoSi in high magnetic fields up to 14 T and constructed detailed B – T phase diagrams for B applied parallel to the tetragonal $[100]$ and $[001]$ axes. The experimental results are presented in Sect. 3; the B – T phase diagram in Sect. 3.1, C in Sect. 3.2, ρ in Sect. 3.3, and M in Sect. 3.4. In addition, we discuss the characteristics of the obtained magnetic phase diagrams in Sect. 4.

2. Experimental Details

Single crystals of CeCoSi were prepared by a Ce/Co eutectic flux method, as described in the previous paper.⁶⁾ A sample piece, named #1, was used for all the measurements, while another sample piece taken from a different batch, named #2, was used only for the M measurements to examine the reproducibility. The dimensions of the thin plate-like samples #1 and #2 are $\sim 2.0 \times 1.0 \times 0.2$ and $\sim 2.0 \times 2.0 \times 0.4$ mm³ for the tetragonal $[100]$ – $[010]$ – $[001]$ axes, respectively.

The C measurements were performed by a thermal-

*hidaka@phys.sci.hokudai.ac.jp

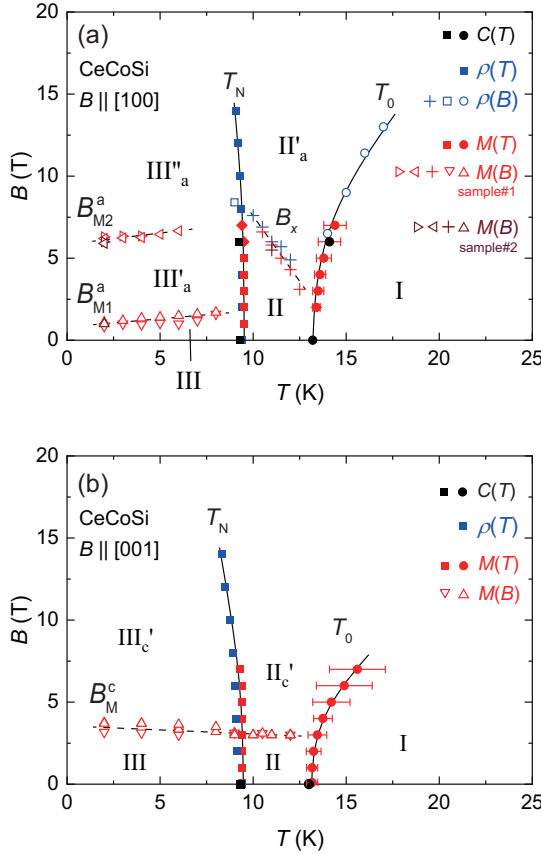


Fig. 1. (Color online) Magnetic field–temperature phase diagrams of CeCoSi constructed on the basis of the present measurements of sample #1 for (a) $B \parallel [100]$ and (b) $B \parallel [001]$. In (a), the data obtained from the M measurements of sample #2 are also plotted. The upward and rightward triangles were determined during the B increasing process in $M(B)$, while the downward and leftward triangles were determined during the B decreasing process. The solid and dashed curves are guides for the eye.

relaxation method in the temperature range of 2–300 K at magnetic fields of $B = 0$ and 6 T using a physical property measurement system (PPMS; Quantum Design). The magnetic field B was applied along [100]. The ρ measurements were performed by a conventional four-probe method in the temperature range of 2–300 K and in the magnetic field range of $-14 - 14$ T using the PPMS. We measured the magnetoresistivity (MR) in two different configurations: a longitudinal MR with electric 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 using a magnetic property measurement system (MPMS; Quantum Design). Magnetic fields were applied along the [100] and [001] directions. The obtained M data for sample #2 are shown in the Sect. 4 of Supplemental Materials (SM).¹⁸⁾

3. Experimental Results

3.1 Magnetic field–temperature phase diagram

First, we show the $B - T$ phase diagrams of CeCoSi constructed on the basis of the present C , ρ , and M measurements for $B \parallel [100]$ and [001] in Figs. 1(a) and 1(b), respectively. The details of each measurement will be given later. The main feature is that these phase diagrams have B -induced regions in the ordered states for $B \parallel [100]$ and possibly also for [001].

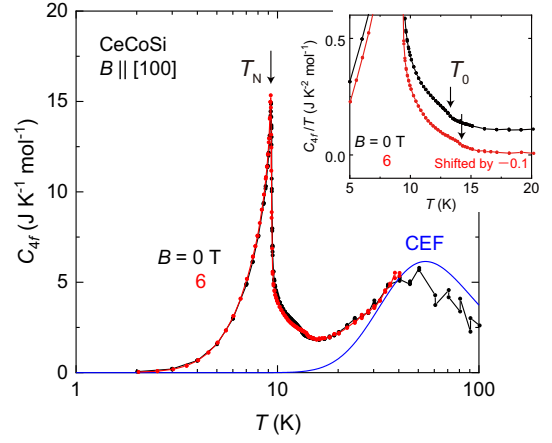


Fig. 2. (Color online) Temperature dependence of C_{4f} in CeCoSi at 0 and 6 T for $B \parallel [100]$. The blue curve represents the calculated CEF Schottky peak.¹⁰⁾ The inset shows the enlarged view of $C_{4f}(T)/T$ near T_0 , where the data at 6 T are shifted vertically for ease of viewing.

Here, we refer to the regions of the HO phase as II and II'_a for $B \parallel [100]$, and as II and II'_c for $B \parallel [001]$, in order from the lowest magnetic field. In addition, we refer to the regions of the AFM phase as III, III'_a, and III''_a for $B \parallel [100]$, and as III and III'_c for $B \parallel [001]$. Region I corresponds to a paramagnetic (PM) phase.

3.2 Specific heat

Figure 2 shows the temperature dependence of C_{4f} in CeCoSi (sample #1) at $B = 0$ and 6 T applied parallel to [100]. Here, C_{4f} is the contribution of 4*f* electrons to the specific heat, which was estimated by subtracting C of LaCoSi at zero field from C of CeCoSi.⁶⁾ The obtained features of $C_{4f}(T)$, which are a λ -type anomaly at T_N , a small jump at T_0 , and a CEF Schottky anomaly at around 40 K, are in good agreement with those reported previously.⁶⁾ T_0 at zero field is estimated to be ~ 13 K in the present sample, which is slightly higher than that of 12 K reported previously.^{6,19)} The blue curve represents the calculated CEF Schottky curve based on the previously suggested CEF level scheme.¹⁰⁾ Applying B of 6 T negligibly affects $C_{4f}(T)$ except for a slight decrease in T_N and an increase in T_0 . The magnitude of the jump at T_0 also changes negligibly despite the increase in 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_x , which separates the II and II'_a regions.

3.3 Electrical resistivity

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 (sample #1) with electric current J applied along the [100] direction and magnetic fields applied along the [100] and [001] directions, respectively. The $\rho(T)$ data at zero field shows no clear anomaly at T_0 , although ρ seems to decrease slightly below T_0 , which is determined from the present $C(T)$ measurement. On the other hand, $\rho(T)$ shows a clear kink anomaly at T_N . The effect of B on T_0 is obscure in both the $\rho(T)$ measurements, while the decrease in T_N for $B \parallel [001]$ is greater than that for $B \parallel [100]$. These results at

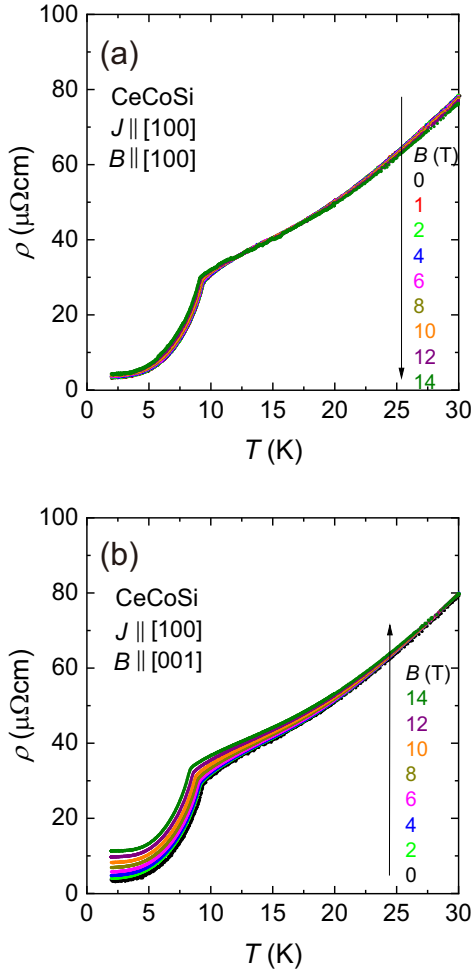


Fig. 3. (Color online) Temperature dependence of electrical resistivity $\rho(T)$ in CeCoSi (sample #1) in magnetic fields up to 14 T for (a) $B \parallel [100]$ and (b) $B \parallel [001]$. Electric current J was applied along the $[100]$ axis in both measurements.

zero field are consistent with the previous report.⁶⁾ In addition, the 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, the $\rho(T)$ curve seems to be nominally affected by B , as can be seen in Fig. 3(a). However, in the longitudinal MR measurements for J and $B \parallel [100]$, the B dependence of ρ shows a clear kink when crossing the phase boundary between the PM and HO phases. Figure 4(a) shows $\Delta\rho(B)/\rho(0)$ obtained from the longitudinal MR measurements in CeCoSi for J and $B \parallel [100]$ at several temperatures between 10 and 20 K in the field range up to +14 T. The data are shifted vertically for clarity in this figure. Here, $\Delta\rho(B)$ and $\rho(0)$ are defined as $[\rho(B) - \rho(0)]$ and ρ at $B = 0$ at a fixed temperature, respectively. At 20 K, which corresponds to the PM state, $\Delta\rho(B)/\rho(0)$ shows a monotonic decrease with increasing B . Below 17 K, one can see a kink anomaly at a high field of ~ 13 T. The corresponding field of the kink anomaly is defined as B_0 [blue open circle in Fig. 1(a)], since B_0 decreases with decreasing temperature down to 14 K and then appears to merge with the $T_0(B)$ curve in the B - T phase diagram.

It is characteristic that the sign of MR in the low B region appears to change gradually from negative in the PM state to positive in the HO state below T_0 of ~ 13 K with decreasing

temperature. The negative MR in the PM state should be due to the suppression of magnetic scattering between the $4f$ and conduction electrons by the external B . On the other hand, the positive MR observed below 13 K would be derived from an electronic state in the HO state. The electronic state in the HO state should be different from that in the PM state, since the XRD measurements have revealed the HO of CeCoSi to be accompanied with a structural change.¹⁷⁾ An anomaly in $\rho(T)$ at T_0 under high pressure, which is suggestive of gap opening, also suggests a change in electronic state because of the HO.^{5,20)} If the positive MR in the HO state mixes with the negative MR in the PM state from above T_0 , the gradual sign change observed in the present study can be explained. This explanation is supported by the XRD measurements, where an increase in structural fluctuation is suggested with decreasing temperature from ~ 20 K toward T_0 .¹⁷⁾ In addition, we found another anomaly above ~ 5 T below T_0 , which increases with decreasing temperature, as can be seen in Fig. 4(a). This result suggests the presence of a high- B region, named II'_a , above region II. Here, the corresponding field of the newly found anomaly below T_0 is defined as B_x .

The results of $\Delta\rho(B)/\rho(0)$ for $B \parallel [100]$ in the AFM state are shown in Fig. 4(b). These $\Delta\rho(B)/\rho(0)$ curves show the positive MR, although the curve changes gradually from downward to upward convex with decreasing temperature. The positive MR in the AFM state may also explain the sign change in MR observed at around T_0 , since the presence of weak AFM fluctuations has been suggested above T_N by the NQR measurements.¹¹⁾ However, the temperature at which the AFM fluctuations develop (~ 12 K) seems low to account for the present sign change in MR. The anomaly observed at 9 K corresponds to the transition field from the AFM phase to the HO phase, defined as B_N [blue open square in Fig. 1(a)]. None of the clear anomalies corresponding to B_{M1}^a and B_{M2}^a , which were observed in the $M(B)$ measurements shown in Sect. 3.4, were observed in the present MR measurements.

Figures 5(a) and 5(b) show the $\Delta\rho(B)/\rho(0)$ curves obtained from the transverse MR measurements for $J \parallel [100]$ and $B \parallel [001]$ below 20 K and between 11 and 20 K, respectively. The raw data measured from $B = -14$ to 14 T are slightly asymmetric with respect to B because of a mixed Hall effect component that is approximately proportional to B . Here, we display the data after the Hall effect component was removed in Fig. 5. The raw $\rho(B)$ data and the estimated Hall effect are shown in Sect. 1 of SM.¹⁸⁾ The $\Delta\rho(B)/\rho(0)$ curves for $B \parallel [001]$ exhibit parabolic behavior with the positive sign at all the investigated temperatures, and no kink anomaly or sign change is observed, which is in contrast to the results of $\Delta\rho(B)/\rho(0)$ curves in the longitudinal MR for $B \parallel [100]$.

To see the characteristics of the transverse MR in CeCoSi, a Kohler plot, $\Delta\rho(B)/\rho(0)$ vs $B/\rho(0)$, is shown in Fig. 5(c). For conventional metals, all Kohler plots from different temperatures are expected to fall on the same curve at low temperatures.^{21,22)} The present results, except for the data below T_N , satisfy the Kohler's rule and show B^2 dependence in this log-log plot, although $\Delta\rho(B)/\rho(0)$ deviates from the B^2 behavior in the high B region above ~ 10 T, as shown in the inset of Fig. 5(b). Such B^2 dependence in the transverse MR can be explained by the scattering due to Lorentz force.^{23,24)} In addition, the satisfaction of Kohler's rule appears to indicate that there is no marked change in the scattering mechanism of

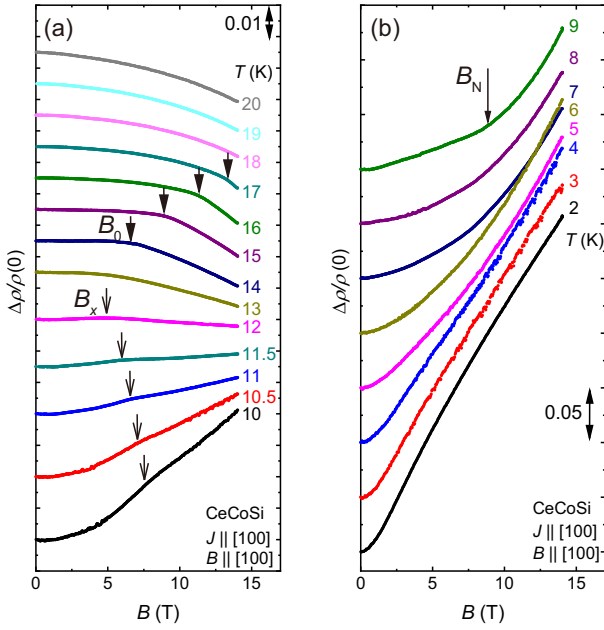


Fig. 4. (Color online) $\Delta\rho/\rho(0)$ in longitudinal MR for CeCoSi (sample #1) plotted as a function of B at several temperatures in the range (a) between 10 and 20 K and (b) below 9 K. Both J and B were applied along the [100] direction. The data are shifted vertically for ease of viewing.

carriers even across T_0 within experimental accuracy; however, it cannot be concluded only from this feature that there is no change in the scattering mechanism between the PM and HO states. The slight change in the MR associated with the HO might be buried in the large positive MR due to Lorentz force, since the amount of change in the transverse MR for $B \parallel [001]$ above T_N is several times larger than that in the longitudinal one for $B \parallel [100]$, where the clear change is observed. The deviation from Kohler's rule and the B^2 behavior below T_N should be attributed to the change in scattering mechanism due to the AFM ordering. It is noted that a similar sign change in the MR has also been revealed by ρ measurements under high pressure²⁰⁾ and for La-substitution systems,²⁵⁾ but it is difficult to compare those previous results with the present results, since those measurements were performed using polycrystalline samples.

3.4 Magnetization

Figures 6(a) and 6(b) show the magnetization process $M(B)$ of CeCoSi (sample #1) for $B \parallel [100]$ and $[001]$ up to 7 T, respectively, measured at temperatures between 2 and 30 K. The indicated data are shifted vertically for clarity in these figures. The respective derivative dM/dB values for $B \parallel [100]$ and $[001]$ are also shown in Figs. 7 and 8, respectively. The steep decrease in dM/dB near zero field, which is observed in all the derivative data, may be due to magnetic impurity. We also confirmed that the temperature dependence of the magnetic susceptibility $[= M(T)/B]$ for both the B directions for sample #1 are in good agreement with those reported previously, as shown in Sect. 2 of SM.^{6,18)} The obtained transition temperatures T_0 and T_N are summarized in the B - T phase diagrams (Fig. 1).

The $M(B)$ curves for $B \parallel [100]$ seem to show simple linear behavior at all the measured temperatures; however, a slight deviation from the linear behavior can be seen at low tem-

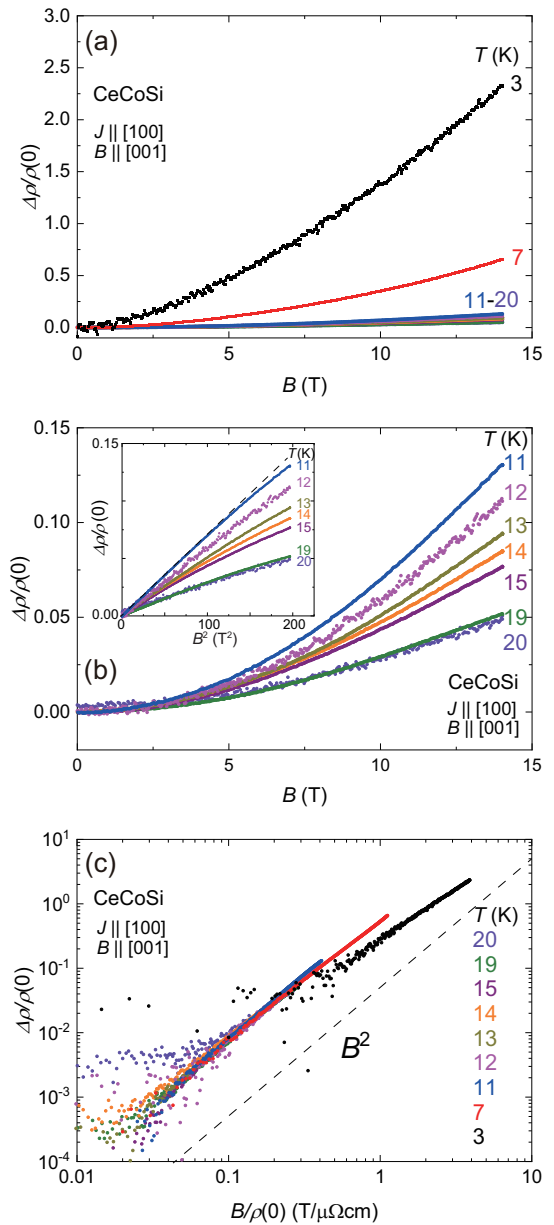


Fig. 5. (Color online) $\Delta\rho/\rho(0)$ in the transverse MR for CeCoSi (sample #1) plotted as a function of B at several temperatures (a) below 20 K and (b) between 11 and 20 K. Here, J was applied along the [100] direction, and B was applied along the [001] direction. The inset of (b) shows the B^2 dependence of $\Delta\rho/\rho(0)$ between 11 and 20 K. (c) shows their Kohler plots at all the measured temperatures. The dashed lines in the inset of (b) and in (c) represent B^2 dependence.

peratures, as seen in the derivative data [Fig. 7]. The dM/dB curves above 16 K are almost constant, whereas at 14 K it starts to increase at around B_0 determined from the present MR measurement. This behavior is consistent with the larger magnetic susceptibility in the HO state than in the PM state. Below $T_0 \sim 13$ K, dM/dB shows a broad maximum at the magnetic field corresponding to B_x . This result also suggests the presence of region II'_a. All the dM/dB curves measured between T_N and T_0 are shown in the Sect. 3 of SM.¹⁸⁾ In addition, the dM/dB curves below T_N show two maximums at around 2 and 6 T accompanied by hysteresis. The hysteresis is observed only below T_N . Here, the magnetic fields where these maximums appear are defined as B_{M1}^a and B_{M2}^a , respec-

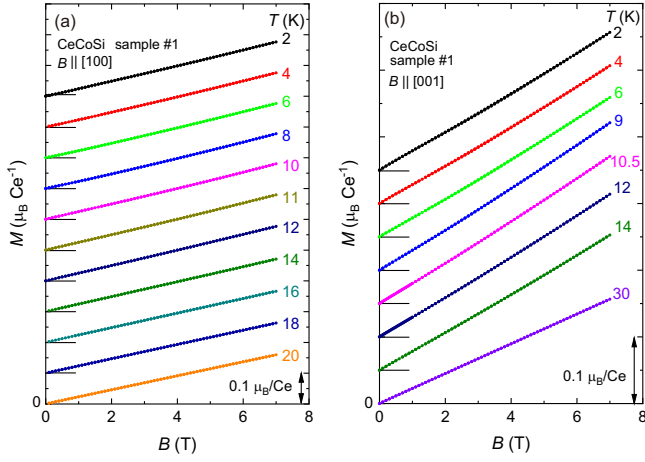


Fig. 6. (Color online) Magnetization curves of CeCoSi (sample #1) at several temperatures for (a) $B \parallel [100]$ and (b) $B \parallel [001]$. The data are shifted by 0.1 and 0.05 μ_B/Ce with respect to each other for ease of viewing in (a) and (b), respectively

tively [red open triangles in Fig. 1(a)]. B_{M1}^a and B_{M2}^a have different values between the B increasing and decreasing processes because of the presence of the hysteresis. These features suggest the presence of B -induced regions, named III'_a and III''_a , in the AFM ordered state.

A similar maximum in the dM/dB curve is observed below T_0 even in the measurements with $B \parallel [001]$, as shown in Fig. 8. In this measurement, the field where the maximum appears, named B_M^c , increases continuously as the temperature decreases. The single maximum above T_N changes to two maximums because of the hysteresis in the AFM state, similarly to the results for $B \parallel [100]$. Here, we named regions above B_M^c in the phase diagram for $B \parallel [001]$ regions II'_c and III'_c , as can be seen Fig. 1(b).

To examine the reproducibility of the results of the $M(B)$ measurements using sample #1, we performed additional $M(B)$ measurements using another sample piece taken from a different batch, named sample #2. The measurement data of sample #2 are shown in Sect. 4 of SM.¹⁸⁾ For $B \parallel [100]$, the anomalies at B_x , B_{M1}^a , and B_{M2}^a are observed in the dM/dB curves even for sample #2, although the steep decrease in dM/dB near zero field due to the magnetic impurity is more pronounced compared with the results for sample #1. The hysteresis is also observed only in the AFM state. On the other hand, we cannot decide whether or not the B_M^c anomaly is present from the measurements for $B \parallel [001]$ using sample #2 owing to the large effect of the magnetic impurity. The small hysteresis observed at 2 K might originate in the presence of B_M^c anomaly. Therefore, we merely point out the possibility of the presence of B -induced regions in the phase diagram for $B \parallel [001]$ at present. Measurements using samples with less impurity and other physical property measurements will be needed to verify the B -induced region.

4. Discussion

We now discuss the characteristics of the B - T phase diagrams constructed in the present study. First, T_0 increases and T_N decreases with increasing B up to 14 T for both B directions, where the B effects on these ordering temperatures are larger for [001] than for [100]. Note that there is no di-

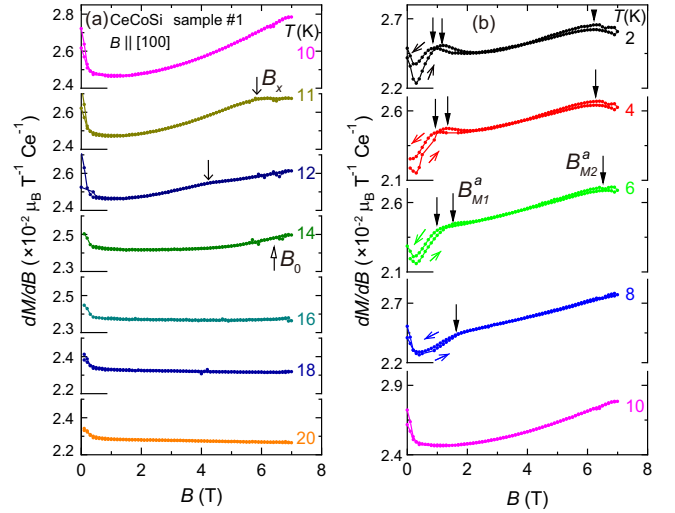


Fig. 7. (Color online) Magnetic field derivative of the magnetization curves dM/dB of CeCoSi (sample #1) for $B \parallel [100]$ (a) between 10 and 20 K and (b) below 10 K. The open arrow in (a) represents B_0 determined from the present MR measurement, and the colored arrows near the hysteresis in (b) represent the B increasing and decreasing processes.

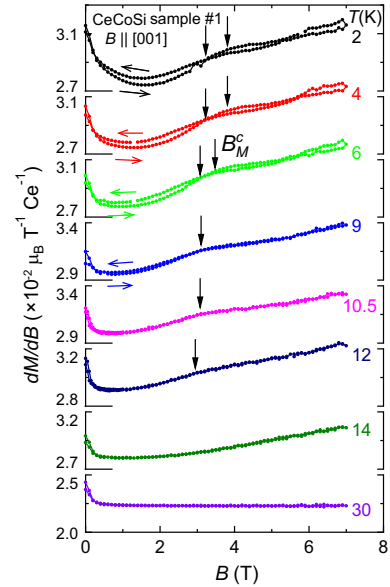


Fig. 8. (Color online) Magnetic field derivative of the magnetization curves dM/dB of CeCoSi (sample #1) for $B \parallel [001]$. The colored arrows near the hysteresis represent the B increasing and decreasing processes.

rect experimental evidence to determine T_0 for [001] above 7 T. However, the HO phase for $B \parallel [001]$ may be induced by B lower than that for [100] at a fixed temperature above T_0 , since dM/dB for [001] at 14 K starts to increase from B lower than that observed for [100] [see Figs. 7(a) and 8]. This anisotropic B dependence of the ordering temperatures should be attributed to the symmetry of the OPs. Such an anisotropic increase in T_0 upon the application of B is similar to a typical characteristic of the electric quadrupolar ordering regardless of whether it is a ferroquadrupolar (FQ) or an AFQ ordering.^{13–16,26,27)} It has been determined that the critical field of the AFM state of CeCoSi is ~ 20 T by high-field M measurements for a polycrystalline sample.⁶⁾ On the other hand, it has not been clarified whether the $T_0(B)$ curve goes towards

absolute zero or disappears under higher magnetic fields at present. This is an important issue to resolve for the elucidation of the ordered state of the HO phase in CeCoSi. Experiments under higher magnetic field are required.

Second, it is suggested that the HO phase of CeCoSi has the B -induced region for $B \parallel [100]$ (and possibly $[001]$). Such a B -induced region would be associated with a change in the symmetry of OP or the alignment of domains by the application of B . Manago *et al.* pointed out the change in OP from hexadecapole or O_{xy} -type AFQ to O_{zx} -type AFQ in the results of the Co-NMR measurements at $B = 1$ T applied along $[100]$.¹¹⁾ Assuming a quadrupole ordering, it is considered that a stable state under high magnetic field is determined by the energy gain due to induced moments, such as magnetic dipole and magnetic octupole moments.²⁸⁾ This possible change in the stable state would cause the suppression of the magnetic scattering in the MR and the small anomaly in the magnetization process observed in the present study. A similar anomaly in the MR accompanied by the emergence of the B -induced phase has also been reported in the AFQ ordering compound PrPb_3 ,²⁹⁾ where the AFQ OP has been suggested to change from O_2^0 to O_2^2 by applying B along the cubic $[100]$.³⁰⁾ Furthermore, it has been reported in the FQ compound $\text{PrTi}_2\text{Al}_{20}$ that the $dM(B)/dB$ curve shows an anomaly originating from the discontinuous switching of the OP induced by the application of B .³¹⁾ It is notable that recent XRD measurements of single-crystalline CeCoSi have also revealed the presence of the B -induced region in the HO phase for $B \parallel [100]$, where the triclinic lattice distortion is absent.¹⁷⁾ Although it cannot be concluded from the present study that B_x merges into T_0 at zero field, which was suggested by the results of the XRD study, the OP in region II may suppress its ordered state under magnetic field, while that in region II'_a may stabilize the state.

The B -induced regions are also observed in the AFM phase in CeCoSi. In the phase diagram for $B \parallel [100]$, the AFM phase is separated into three regions by B_{M1}^a and B_{M2}^a . The B_{M1}^a anomaly should be independent of the presence of the II'_a region, while B_{M2}^a appears to be connected to B_x above T_N . These B -induced anomalies in the AFM phase have also been pointed out from the previous XRD measurements, although the B_{M2}^a determined by XRD (~ 8 T) is higher than that determined in the present study.¹⁷⁾ The XRD measurements suggested that preferable triclinic structural domains are selected at B_{M1}^a , and the triclinic distortion disappears above B_{M2}^a .¹⁷⁾ The hysteresis in the magnetization process, which is observed only in the AFM phase, suggests the presence of metastable states in the structural domain alignment. On the other hand, the possible presence of the II'_c and III'_c regions for $B \parallel [001]$ might also be explained by the domain arrangement. Note that a similar magnetic phase diagram has been constructed on the basis of the XRD measurements for $B \parallel [110]$.¹⁷⁾

The magnetic structure of the AFM phase in CeCoSi is still controversial. The magnetic structure at zero field has been proposed to be a simple collinear one with the magnetic moments pointing along the $[100]$ direction on the basis of 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 diagrams obtained in this study, the AFM

magnetic structure may not be so simple one as proposed by Nikitin *et al.*¹⁰⁾ Furthermore, if the antiferro-type ordering at Ce on-sites with $\mathbf{q} = 0$ occurs, the space-inversion symmetry at the midpoint between Ce ions is broken, resulting in the activation of the Dzyaloshinskii–Moriya (DM) interaction. The DM interaction will induce the tilting of magnetic moments in the AFM state. Taking these into consideration, the direction of magnetic moments is expected to be changed by the application of small B . The relationship between the possible change in the direction of magnetic moments and the alignment of the structural domains upon the application of B also must be clarified.

Finally, the B – T phase diagrams of CeCoSi could be explained by the successive phase transitions of the electric quadrupole and magnetic dipole orderings; however, the OP in the HO state has not yet been settled, including the antiferro or ferro type. Most compounds showing the quadrupole ordering of $4f$ electrons have the quadrupole degrees of freedom in their CEF GS, such as a Γ_8 quartet for the Ce^{3+} ion and a non-Kramers Γ_3 doublet for the Pr^{3+} ion.^{15,32,33)} 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 ~ 100 K.^{6,10)} This CEF splitting seems to be too large to drive the quadrupole ordering of the local $4f$ electron at T_0 of 13 K. The obscure anomaly at T_0 in the bulk properties of CeCoSi, such as $C(T)$, $M(T)$, and $\rho(T)$, is also a feature different from that found in the typical compounds showing the quadrupole ordering of the localized $4f$ electron.^{14,16,29,30,34)} In particular, the jump at T_0 in $C(T)/T$ of CeCoSi is considerably small, whereas the released entropy at T_N is large ($\sim 0.8 R \ln 2$), suggesting the magnetic ordering of the $4f$ electron. It is noteworthy that the magnitude of the jump at T_0 changes negligibly even at a high magnetic field of 6 T. This robustness is in contrast to 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 in the HO phase 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 those on lattice distortion and the B – T phase diagram under higher B and high pressure, are needed and are now in progress.

5. Summary

We performed C , ρ , and M measurements in single crystals of CeCoSi under B up to 14 T applied parallel to the tetragonal $[100]$ and $[001]$ axes. For $B \parallel [100]$, a small jump at T_0 in $C(T)/T$ changes negligibly upon applying B of 6 T in spite of an increase in T_0 . In the longitudinal MR measurements for $B \parallel [100]$, we found a sign change in the MR from negative to positive across T_0 and a B -induced anomaly at B_x below T_0 . The $M(B)$ curves for $B \parallel [100]$ also exhibit small B -induced anomalies in both the HO and AFM states. These results suggest the presence of B -induced regions not only in the HO

phase but also in the AFM phase in B - T phase diagrams for $B \parallel [100]$, which is in good agreement with the phase diagram constructed on the basis of the previous XRD measurements up to $B = 6$ T.¹⁷⁾ The presence of the B -induced regions may be a consequence of a change in the symmetry of the OP or domain alignment upon the application of B , which could be a clue to unraveling the mystery of the HO and the magnetic structure of the AFM state. Furthermore, a possibility that the B - T phase diagram for $B \parallel [001]$ also has the B -induced regions in both the ordered phases is suggested from the present M measurements. However, the transverse MR for $B \parallel [001]$ shows no anomalies and satisfies Kohler's rule above T_N . Further verification is required to establish the B -induced regions for $B \parallel [001]$.

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