Unusual Nonmagnetic Ordered State in CeCoSi Revealed by $^{59}$Co-NMR and NQR Measurements

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We performed $^{59}$Co nuclear magnetic and quadrupole resonance (NMR and NQR) measurements under pressure on a single-crystalline CeCoSi, which undergoes an unresolved phase transition at $T_0$. The NQR spectra clearly showed that the phase transition at $T_0$ is nonmagnetic, but any symmetry lowering at the Co site was not seen irrespective of the feature of second-order phase transition. By contrast, the NMR spectra were split by the induced magnetic field perpendicular to the external magnetic field. These results show that the phase below $T_0$ is not a simple paramagnetic state but is most likely electric multipolar ordered state of Ce 4$f$ electrons. The development of the Kondo effect by applying pressure is thought to be crucial to stabilize this state and to show novel features beyond commonality of tetragonal Ce-based systems.

Physical properties of solids are influenced intricately by degrees of freedom of electrons, that is, charge, spin, and orbital, through their mutual couplings and many-body interactions of electrons. Phase transition characterized by an order parameter is one of the demonstrations of their influence; therefore, it is a fundamental yet profound phenomenon. Rich interactions in solids induce various types of phase transitions; hence, they are attractive in condensed matter physics.

Such diversity yields at times a mysterious ordered state. A well-known example is the “hidden order” state in the 5$f$-electron system URu$_2$Si$_2$ [1, 2]. It is a second-order phase transition with a symmetry reduction; however, the crystallographic symmetry of the ordered state is still controversial [3–6]. Several researchers have attempted unmasking the order parameter in URu$_2$Si$_2$ for three decades because it is just a fundamental question in condensed matter physics; the mechanism through which degrees of freedom of electrons can affect physical properties of solids.

The 4$f$-electrons system CeCoSi is a potential example exhibiting an extraordinary order parameter. It crystallizes in the tetragonal $P4/nmm$ ($D_{2d}$, No. 129) space-group symmetry with the CeFeSi-type structure [7]. The spacial inversion symmetry is locally absent at the Ce site, whereas the crystal structure has the global inversion symmetry. The crystal electric field (CEF) ground state has been reported as the $\Gamma_7 (\pm 0.306 \pm 5/2 \pm 0.95 \pm 3/2)$ Kramers doublet, and the first excited state is separated from it by $\sim 100 \text{ K}$ [8]. It has been established that an antiferromagnetic (AFM) transition occurs at the Néel temperature $T_N = 9.4 \text{ K}$. The transition is of second-order [9], and the Ce moments with sizes of $m_{\text{Ce}} \sim 0.37(6)\mu_B$ are aligned along the [100] axis with a $q = 0$ structure, as revealed by a neutron scattering study [8]. Another phase, which is a matter of interest, has been initially reported to emerge under pressure below $\sim 40 \text{ K}$ at $\sim 1.5 \text{ GPa}$ [10]. The first unresolved issue of this phase is its intrinsic pressure phase diagram. Contrary to some reports [8, 10], a study on single-crystalline samples proposed that this “pressure-induced ordered phase” already exists at ambient pressure below $T_0 = 12 \text{ K}$ [11]. The phase below $T_0$ at lower pressures seems to continuously connect to the pressure-induced phase [11, 12]. However, the anomaly at $T_0$ at ambient pressure is not sufficiently large to convince a phase transition. Therefore, microscopic measurements are desired to reveal whether the phase transition at $T_0$ is intrinsic or not at ambient pressure. The second unresolved issue is the order parameter below $T_0$. It seems different from usual AFM states, as deduced from an enhancement by the magnetic field [10, 11]. There have been various suggestions for the origin of this phase, as follows: the spin-density-wave order of Co 3$d$ electrons, metaorbital transition, and antiferroquadrupolar (AFQ) ordering [10–12]; however, the order parameter remains unresolved.

In this Letter, we present the results of $^{59}$Co nuclear magnetic and quadrupole resonance (NMR and NQR) measurements on high-quality single-crystalline CeCoSi samples to clarify the above-mentioned issues. The combined NMR and NQR results revealed the intrinsic phase diagram, where the objective phase was present even at ambient pressure. In the ordered state, there is no clear indication of symmetry reduction at the Co site under zero field, whereas the NMR spectra split below $T_0$ when the magnetic field tilted from the $[100]$ axis was applied. This NMR anomaly can be interpreted by the emergence of the induced magnetic field perpendicular to the external field. Present results suggest an unusual nonmagnetic ordered state that is most likely an electric multipole ordered state in CeCoSi.

Plate-shaped single-crystalline CeCoSi samples ($\sim 3 \times 4 \times 0.5 \text{ mm}^3$) were grown using the Ce/Co eutectic flux method, as described in Ref. [11]. The $^{59}$Co ($I = 7/2$) NMR and NQR measurements were performed in the temperature range 1.4–300 K using a standard spin-echo method. The NMR spectra were obtained under a field of 1 T near the $[100]$ direction, and its angle was deduced from the frequencies of the spectra above $T_0$. The local symmetry of the Co site in the $P4/nmm$ space group is $4m2$ with four-fold improper rotational symmetry. Hydrostatic pressure was applied up to 2.35 GPa on another sample using a piston-cylinder-type cell with Daphne 7474 as a pressure-transmitting medium. The pressure was determined from the superconducting transition temperature of a Pb sample inside the cell. A LaCoSi sample consisting of
FIG. 1. (Color online) (a–c) Temperature dependence of the 59Co NQR spectra of CeCoSi at ν3 = 3νQ site without a field under a pressure of (a) 0, (b) 1.09, and (c) 1.52 GPa. The spectra at each temperature are shifted vertically. (d) Temperature and pressure dependence of νQ of CeCoSi and that of LaCoSi at ambient pressure. The vertical arrows indicate T0 determined by NMR measurements, which detected it even at ambient pressure. The dashed line for LaCoSi indicates the conventional temperature dependence of νQ.

single-crystalline pieces was also measured by NQR at P = 0 as a reference system.

The NQR spectra are sensitive to both the magnetic and electric anomalies and are suitable for probing the nature of the ordered state. Figures 1(a)–1(c) show the temperature dependence of the NQR spectra above T_N at the ν3 = 3νQ (±5/2 ↔ ±7/2) site at 0, 1.09, and 1.52 GPa. The value of the quadrupole frequency νQ was 2.09 MHz at P = 0 and 20 K. The results on other pressures are shown in the Supplemental Materials. The NQR spectra did not split nor broaden, although they showed a shift at T0. As shown in the temperature dependence of νQ in Fig. 1(d), the kink of νQ is clearer at higher pressures, and it is invisible at ambient pressure. The kink is not a necessary condition for the phase transition, and its presence at ambient pressure is proved by NMR measurements mentioned later. The absence of splitting or broadening NQR spectra demonstrates that the internal field is absent at the Co sites for T_N < T < T0 in the entire pressure range. This clearly excludes the magnetic ordering of Co 3d moments below T0. Our results also indicate that all the Co sites remain equivalent below T0 while maintaining a local tetragonal symmetry, that is, a tetragonal crystal structure. If one considers a possibility of the magnetic ordering of Ce 4f moments, the only explanation for the NQR result is a cancellation of the internal magnetic field at the Co site, which is surrounded by four Ce ions. The transition to the underlying AFM state at T_N is of second-order, and this AFM state with q = 0 does not break the translational symmetry of the crystal above T0. Then, the intermediate ordered state in T_N < T < T0 should maintain the same translational symmetry, that is, the propagation vector is q = 0. For the q = 0 structure, the internal field is canceled only when the staggered Ce moment is along the [001] axis. This possibility is excluded by the increase of the susceptibility along this axis below T0. Thus, we concluded that the ordered phase below T0 is nonmagnetic with one tetragonal Co site. The unusual field response explained later also excludes the possibility of the magnetic state and yet indicates that this phase is not a simple paramagnetic state.

The temperature dependence of νQ usually obeys a conventional monotonous behavior νQ(T) = νQ(0)(1 − αT^{1.5}) owing to the lattice expansion and vibration, as observed in LaCoSi. In contrast, the νQ(T) in CeCoSi deviates from this behavior above T0, and the deviation becomes remarkable as the pressure increases. Such behavior has been observed in some 4f-electron systems and discussed to originate from a CEF splitting, a valence change of the 4f ion, or the Kondo effect. The distinct pressure dependence in CeCoSi indicates that such multiple effects influence νQ at the Co site through the pressure-enhanced hybridization between the 4f electron and conduction electrons.

Figure 2 shows the Ce-4f part of the nuclear spin-lattice relaxation rate 1/T1 measured by the NQR at H = 0. The 1/T1 has a Co 3d component, and it was subtracted using the

FIG. 2. (Color online) Temperature dependence of 59Co NQR nuclear spin-lattice relaxation rate 1/T1 of CeCoSi from the Ce-4f electrons at H = 0 under several pressures. The 4f part was obtained by subtracting the 1/T1 value of LaCoSi. The vertical arrows indicate T0 determined by NMR results. Inset (left panel): 1/T1 of CeCoSi at ambient pressure before subtraction as well as that of LaCoSi. The dashed line for LaCoSi shows the Korringa relation 1/T1 ∝ T in the normal metal.
result of LaCoSi (see the inset of the left panel of Fig. [3]). The $1/T_1$ divided by temperature is shown in Supplemental Materials [13]. The $1/T_1$ of LaCoSi shows the weakly-correlated Pauli paramagnet corresponding to a previous report [20]. The absence of phase transition in LaCoSi is consistent with the interpretation that the phase below $T_0$ originates from Ce 4f electrons. No divergent behavior was detected near $T_0$ in $1/T_1$ in CeCoSi, indicating the absence of the magnetic critical fluctuations. A clear drop was found at $T_0$ only at 2.03 GPa. This may correspond to the gaplike anomaly in the electric resistivity above $\sim 1.5$ GPa [10] and suggest the decrease of the density of states. Around $T_N$, $1/T_1$ is expected to detect the magnetic fluctuations perpendicular to the [001] axis [13]. $1/T_1$ diverged owing to the critical slowing down of the magnetic fluctuations at ambient pressure (see also Fig. 7 in the Supplemental Materials [13]). However, the divergence of $1/T_1$ is suppressed with increasing pressure. This is not expected with the magnetic structure of $m \parallel [100]$. Two possibilities are considered to interpret this result. One is that the magnetic moment is tilted along the [001] axis under pressure. Another is that the magnetic fluctuation is suppressed as the ordered state below $T_0$ gets stabilized. The $1/T_1$ significantly above $T_0$ shows the localized Ce 4f electrons ($1/T_1 = \text{const.}$) at 1.52 GPa or below. Meanwhile, $1/T_1$ starts to decrease from higher temperatures than $T_0$ at 2.03 and 2.35 GPa. Such an itinerant behavior owing to coherent Kondo effect in $1/T_1$ is also seen in some heavy-fermion systems including CeCu$_2$Si$_2$ [21][22]. The $1/T_1$ result, combined with the $v_0$ behavior, indicate an enhancement of the Kondo effect by pressure.

Further information on the ordered state is provided by the spectra measured under a magnetic field. Figure 3(a) shows the full set of the NMR lines at ambient pressure at 10 K below $T_0$ = 12 K with a field strength of $\mu_0H = 1.0$ T in addition to the results of 20 K. Here, $\theta = 87.8^\circ$ and $90^\circ$ are the field angles from the [001] to [100] axes. At 20 K, seven NMR lines were observed owing to the nuclear quadrupole interaction of $I = 7/2$ $^{59}$Co nucleus. Meanwhile, at 10 K, the third satellite at the lowest frequency split when the field was tilted from the [100] axis, clearly indicating the symmetry reduction below $T_0$. The two-split peaks merged just when $H \parallel [100]$, which was consistent with the NQR data and suggesting that the crystallographic Co site remains one site below $T_0$. Similar split and merging of the spectra were observed when the magnetic field is around [001] axis (not shown).

Figures 3(b)–3(d) show the temperature dependence of the NMR third satellite line with the field of $\mu_0H = 1.0$ T slightly tilted from the [100] axis under pressures of 0, 1.09, and 1.52 GPa. The results under other pressures are shown in Supplemental Materials [13]. The spectra started to split at $T_0$ at all pressures, and the value of $T_0$ corresponds with the previous reports [11][12]. This is the first microscopic evidence for the phase transition at $T_0$ at ambient pressure. Careful measurements just below $T_0$, especially at ambient pressure, indicate that the transition is of second-order [13]. Three peaks were observed at intermediate temperatures at 1.52 GPa and other pressures [13], although it is unclear whether this is intrinsic or not. Here we assume the two-peak structure to be intrinsic because it is also observed at ambient pressure, where the stress or inhomogeneity owing to pressure is free.

The NMR line split is remarkable at the low-frequency third satellite line and disappears for $H \parallel [100]$. This situation is reproduced only when the induced magnetic field $H_{ind}$ is perpendicular to the external field, as shown in Fig. 3(e). The blue solid and dashed lines in Fig. 3(a) indicate the simulated NMR frequencies, where $\mu_0H_{ind,c} \sim \pm 15$ mT along the [001] axis are adopted. When the external field $H_{ext}$ is tilted from [100] to the [001] axis, the total field at two Co sites, $H_{ext} + H_{ind}$, differs from each other, leading to the splitting of the NMR frequency. The field $\mu_0H_{ind,z} \sim \pm 15$ mT is absent.

![Fig. 3. (Color online) (a) $^{59}$Co NMR spectra of CeCoSi at ambient pressure at 10 and 20 K with the field $\mu_0H = 1.011$ T and angles $\theta = 87.8^\circ$ and $90^\circ$. The blue solid and dashed lines indicate the simulated peak frequencies at $T = 10$ K assuming the staggered field of $\sim \pm 15$ mT along the [001] axis. The vertical arrow indicates the central (1/2 $\leftrightarrow$ −1/2) line, whereas the vertical black dashed line indicates the frequency of $K = 0$ of the central line. (b–d) Temperature dependence of the spectra under pressures of (b) 0, (c) 1.09, and (d) 1.52 GPa with $\mu_0H = 1.0$ T slightly tilted from the [100] axis. The spectra are shifted vertically with an offset proportional to the temperatures. The horizontal arrows indicate $T_0$. (e) Schematic of the induced field $H_{ind}$ under the external field $H_{ext}$ at the Co sites below $T_0$. Only the [001] components of $H_{ind}$ are drawn for simplicity.](image-url)
in the NQR spectra, and thus, this is induced by the external field. Such an induced field cannot be explained by a simple paramagnetic response of Ce $4f$ magnetic moment [13]. Notably, this excludes the possibility that the internal field at the Co site is canceled out in the AFM alignment of the Ce moments because tilting of the AFM moments under an external field yields a similar response to the paramagnetic response without splitting of the NMR line.

Figure 4 shows the temperature–pressure phase diagram of CeCoSi determined by our NMR and NQR results. The phase transition at $T_0$ at ambient pressure was unambiguously confirmed to be intrinsic from the microscopic point of view. Our results clearly demonstrate that second-order transitions occur successively across $T_0$ and $T_N$. The pressure dependence of $T_0$ is reminiscent of the Doniach-type phase diagram, implying that the $c$–$f$ hybridization assists the stabilization of the ordered state at lower pressures. Two ordered phases are suppressed with increasing pressure, accompanied by the development of the Kondo effect, and the nonmagnetic ground state is realized in the pressure range of 1.4–2.15 GPa.

Our NMR and NQR results limit possible order parameters in CeCoSi as follows: in $T_N < T < T_0$, they exclude magnetically ordered states arising from Ce-$4f$ and Co-$3d$ electrons. Nonmagnetic ordered states arising from Co-$3d$ electrons, such as a charge density wave (CDW) or orbital ordering are also unlikely. If the CDW transition occurs, the spectra will be split into several sites corresponding to the superlattice formation. Similarly, if the phase transition lifts the Co-$3d$ orbital degeneracy protected by local tetragonal symmetry, orthorhombic transition is essential similar to an electronic nematic state in Fe pnictide systems [23]. The on-site NMR and NQR results did not show the corresponding symmetry reduction. As an ordered state of nonmagnetic Ce origin, the “metaorbital” transition [24], across which the occupancy of the Ce-$4f$ electrons changes steeply, is proposed [10]; however, it does not correspond with the second-order transition with a symmetry reduction. The remaining possibility that should be considered is the contribution of electric degrees of freedom of Ce $4f$ electrons; that is, an electric multipole ordering. The CEF ground state of tetragonal CeCoSi is a Kramers doublet, but the AFQ ordering is possible if the state including the first-excited level possesses a large interlevel interaction [25], which is most likely enhanced by the Kondo effect. Quadrupolar degrees of freedom involving CEF excited states are also known in PrOs$_4$Sb$_{12}$ [26, 27] and CeTe [28].

Before deepening this discussion, we provide a general symmetry consideration, as discussed for the hidden-order state in URu$_2$Si$_2$ [29, 30]. Because the transition to the nonmagnetic state across $T_0$ in CeCoSi is second-order, the space group below $T_0$ must be one of the subgroups of the room-temperature phase of No. 129 ($P4/nmm$). Moreover, the underlying AFM state orders to $q = 0$ structure, preserving the translational symmetry [8] while excluding the possibility of superlattice formation above $T_N$. Thus, the possible maximal subgroups are as follows: No. 59 ($Pmmm$), 85 ($P4/n$), 90 ($P4_212$), 99 ($P4mm$), 113 ($P4_2/nm$), and 115 ($P4/nm$) [13, 31]. Because the Co site remains one site below $T_0$, the space group with two Co sites, namely, No. 115, is unlikely. The breaking of the four-fold symmetry was not detected at the Co site, which contradicts No. 59, 90, and 99 with two-fold symmetry at the Co site. Therefore, the space group No. 85 or No. 113 is preferable for the state below $T_0$ in CeCoSi. An interesting feature is that the symmetry reduction to No. 85 or No. 113 does not require the shift of the atomic positions [13, 31], that is, it can be satisfied by symmetrical change of electronic configurations of the Ce ions. If that is the case, the lattice distortion is triggered by the weak coupling to the electrons, and the detection of the symmetry change may not be straightforward in X-ray measurements. This would happen in URu$_2$Si$_2$ [29, 30]. Moreover, the No. 113 lacks global inversion symmetry; therefore, experimental methods that can observe the splitting of bands will be effective to confirm this.

A clue to understand the origin of this phase is the unusual field response, i.e., the induced field perpendicular to the external field. Such a behavior is reminiscent of an AFQ state [32, 33], as observed in ferro- or antiferroquadrupolar systems CeB$_6$ [34], PrFe$_2$P$_12$ [35, 36], PrTi$_2$Al$_{20}$ [37], and NpO$_2$ [38]. Therefore, it is reasonable to consider the ordered state in CeCoSi as an AFQ state. Along this line of thought, a crucial point is consistency between the experiment and theoretical suggestion [25]. In the case of multipolar states, the space groups No. 85 and 113, suggested by the NQR result, correspond to the hexadecapolar and $O_{2x}$-type AFQ states, respectively. The symmetry of the Ce site reduces to four-fold symmetry without mirror operations $(4_\gamma)$ in the No. 85 and two-fold symmetry $(2/mm)$ in the No. 113 space group [13]. Meanwhile, identification of the AFQ order parameter is possible in principle from the NMR-line splitting by a theoretical work [39]. For example, the NMR line can split in the $O_{2x}$-type AFQ state when $H \perp [010]$, except for $H \parallel [100]$ and $H \parallel [001]$. Therefore, the induced field detected by our NMR suggests the $O_{2x}$-type AFQ state. In the case of $O_{xy}$ type, which is proposed by the zero-field result, the line splitting does not occur by the component along [001] of the field.
Thus, we need to resolve this discrepancy between zero- and finite-field results to settle the origin of the ordered state. A point to be considered is the switching of the order parameter under field, as in some quadrupole systems such as CeB₆ [40] and PrTi₂Al₃ [41]. Such a signature has not been observed thus far in CeCoSi, but investigations for the field-induced switching may unravel this issue. Another point is the lack of local inversion symmetry at the Ce site. In this case, odd-parity multipoles, such as electric octapole, are active in principle through the asymmetric spin-orbit interaction at the Ce site, but the mechanism through which this effect influences the field response is unknown. In any case, our results capturing a peculiarity of the ordered state in CeCoSi will offer theoretical and further experimental challenges for the complete elucidation of the order parameter.

In conclusion, we have performed single-crystalline NMR and NQR measurements to investigate the unresolved ordered state in CeCoSi. The absence of any signature of symmetry reduction in the ⁵⁹Co-NQR spectra indicates that the ordered phase below T₀ is nonmagnetic and originates from Ce ⁴f electrons. An unusual field response, proved by the NMR-line splitting, characterizes the extraordinary ordered state, indicating that it is most likely the electric multipole state. Our results show that CeCoSi undergoes two types of second-order phase transitions with different symmetry lowerings, and the nonmagnetic phase can be the ground state above ~ 1.4 GPa. It is interesting to consider why CeCoSi differs from other non-cubic systems. As an idea, we expect that parity mixing by absence of the local inversion symmetry at the Ce site may be a key factor to induce this peculiar behavior in CeCoSi. In any case, CeCoSi is a novel example offering profound physics originating from the ⁴f⁴ state.

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