Evidence for a Novel State of Superconductivity in Noncentrosymmetric $CePt_3Si$: A ^{195}Pt-NMR Study

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We report on novel antiferromagnetic (AFM) and superconducting (SC) properties of noncentrosymmetric $CePt_3Si$ through measurements of the ^{195}Pt nuclear spin-lattice relaxation rate $1/T_1$. In the normal state, the temperature (T) dependence of $1/T_1$ unraveled the existence of low-lying levels in crystal-electric-field multiplets and the formation of a heavy-fermion (HF) state. The coexistence of AFM and SC phases that emerge at $T_N = 2.2$ K and $T_c = 0.75$ K, respectively, takes place on a microscopic level. $CePt_3Si$ is the first HF superconductor that reveals a peak in $1/T_1$ just below T_c and, additionally, does not follow the T^3 law that used to be reported for most unconventional HF superconductors. We remark that this unexpected SC characteristic may be related to the lack of an inversion center in its crystal structure.

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In almost all previous studies on superconductors, it was assumed that the crystal has an inversion center, which makes it possible to separately consider the even (spin-singlet) and odd (spin-triplet) components of the superconducting (SC) order parameter (OP) [1,2]. For example, Ce-based heavy-fermion (HF) superconductors $CeCu_2Si_2$ and $CeMIn_5$ (M = Co, Rh, Ir) have a centrosymmetry in the crystal structure. Although this is the case in most superconductors, there are some exceptions. Very recently, Bauer *et al.* discovered a new HF compound $CePt_3Si$ that does not have centrosymmetry or an inversion center [3]. The crystal structure of $CePt_3Si$ belongs to the space group $P4mm$ (No. 99), being isostructural with the ternary boride compound $CePt_3B$ as shown in the inset in Fig. 1 [3,4]. $CePt_3Si$ exhibits antiferromagnetic (AFM) order below $T_N = 2.2$ K and undergoes a SC transition at $T_c = 0.75$ K that was probed by the measurements of electrical resistivity $R(T)$ and specific heat C_p. As for the AFM ordering, $R(T)$ does not show a pronounced anomaly at $T = T_N$, but C_p/T exhibits there a distinct peak [3]. The entropy release at T_N is estimated to be as small as $\Delta S = 0.22R\log 2$. This result refers to the development of Kondo-like interaction between $4f$ electrons and conduction electrons below 10 K that is evidenced from an almost logarithmic increase of C_p/T below 10 K as well. With respect to the SC characteristics, only a small jump of C_p/T at T_c was found ($\Delta C_p/\gamma T_c \sim 0.25$), but an enhanced value of Sommerfeld coefficient $\gamma \sim 390$ mJ/mol K^2 suggests that HF superconductivity is realized in this compound. Furthermore, H_{c2} at low T exceeds the usual Pauli paramagnetic limiting field, indicative of a possibility of spin-triplet pairing. However, from a general argument that the lack of an inversion center does not always allow stable spin-triplet pairing, a mixing of spin-singlet and spin-triplet pairing was proposed for $CePt_3Si$ [3].

Very recently, neutron scattering experiments elucidated magnetic properties on $CePt_3Si$ [5]. An AFM Bragg reflection was deduced at a wave vector $\mathbf{Q} = (0, 0, 1/2)$ and $(1, 0, 1/2)$, indicating that Ce-$4f$-derived magnetic moments $\sim 0.3\mu_B$/Ce at $T = 1.8$ K align ferromagnetically in the basal plane and stack antiferromagnetically along the c axis. Its size is much smaller than the value expected from a Ce^{3+} crystal electric field (CEF) ground state with either a Γ_7 or Γ_6 Kramers doublet. This suggests that Kondo-like interactions become effective, reducing the size of the ordered moments with

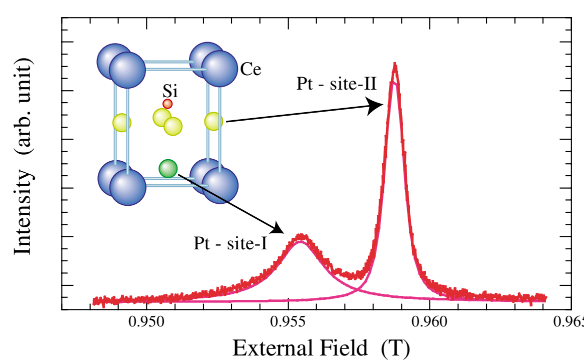

FIG. 1 (color online). The ^{195}Pt-NMR spectrum for the oriented powder along the c axis parallel to magnetic field (H) at 4.2 K and $f = 8.9$ MHz ($H \sim 1$ T).

respect to the simple localized picture. Consistency is found with the results of specific-heat measurements that indicate only a small entropy release at T_N as mentioned above [3]. The neutron scattering experiments also provided information for a CEF energy scheme [5]. The most remarkable finding is that well defined CEF excitations were observed in this compound, although $4f$ electrons are hybridized with conduction electrons to form heavy quasiparticles. A similar observation was reported for the first Pr-$4f^2$-derived HF superconductor $PrOs_4Sb_{12}$ [6]. In this case, it was revealed from band structure calculations and de Haas–van Alphen effect measurements that the $4f$ electrons are almost localized [7].

In order to gain insight into the possible OP symmetry of noncentrosymmetric $CePt_3Si$, several theoretical works have been put forward so far. Frigeri *et al.* have shown that, in contrast to common belief, spin-triplet pairing is not entirely excluded in such systems [8]. Furthermore, the Pauli paramagnetic limit in $H_{c2}(0)$ was analyzed for both spin-singlet and spin-triplet pairing. $CePt_3Si$ has the possibility of a p-wave spin-triplet pairing state [$\boldsymbol{d}(\boldsymbol{k}) = \hat{\boldsymbol{x}}k_y - \hat{\boldsymbol{y}}k_x$] that can explain the absence of the Pauli paramagnetic limit reported by Bauer *et al.* On the other hand, noting that its superconductivity emerges under the background of AFM ordering, it seems more natural to assume a spin-singlet type of pairing, and Frigeri *et al.* argued that the Pauli paramagnetic limit is rendered less effectively by the presence of spin-orbit coupling arising from the broken inversion symmetry. Band structure calculations revealed that a possible gap structure of $CePt_3Si$ depends on the dimensionality of the SC OP, and, if the SC OP corresponds to a one-dimensional representation, then the gap has line nodes where the Fermi surface crosses the high-symmetry planes or the boundaries of the Brillouin zone [9].

In this Letter, we report on a microscopic study of $CePt_3Si$ via measurements of nuclear magnetic resonance (NMR) of ^{195}Pt. Our aim is to clarify novel magnetic and SC characteristics inherent to $CePt_3Si$, the first HF superconductor without inversion symmetry, and provide microscopic evidence for the coexistence of antiferromagnetism and superconductivity.

We used polycrystalline and single crystals of $CePt_3Si$ for the ^{195}Pt-NMR measurement. Polycrystalline samples were synthesized by high frequency melting. Single crystals were successfully prepared by both the pulling method in a tetra-arc furnace and mineralization [5]. For the ^{195}Pt-NMR measurement, the samples are crushed into powder to make rf field penetrate easily.

Figure 1 displays the ^{195}Pt-NMR spectrum at 8.9 MHz for powder oriented along the c axis parallel to H. $CePt_3Si$ has two inequivalent crystallographic Pt sites (see the inset in Fig. 1). One Pt site is surrounded by four Ce atoms within the ab plane, labeled as site I; the other one is labeled as site II. The respective full width at half-maximums (FWHMs) in the Pt-NMR spectral shape are as small as 25 Oe at site I and 8 Oe at site II, assuring that the samples are well characterized.

In the paramagnetic (PM) state above $T_N = 2.2$ K, the Pt-NMR spectra at sites I and II exhibit positive values of Knight shift but no significant changes. Below T_N, however, their FWHMs actually start to increase, associated with the appearance of an internal field due to the onset of AFM order. As a result, the spectra from sites I and II overlap below T_N. Note that the peak in the spectrum below T_N is attributed mainly to spectral weight from site II.

Since the ^{195}Pt nuclei has a nuclear spin $I = 1/2$, it follows a simple exponential form given by $[M(\infty) - M(t)]/M(\infty) = \exp(-t/T_1)$, where $M(\infty)$ and $M(t)$ are the nuclear magnetization for the thermal equilibrium condition and at a time t after the saturation pulse, respectively. $1/T_1$ is uniquely determined by a single component above T_c. At temperatures well below T_c, however, two components appear in T_1: a long component is attributed to an intrinsic relaxation, whereas the short one arises from the presence of vortex core induced by applying H.

Figure 2 presents the T dependence of $1/T_1T$ at site I at $f = 8.9$, 18.1, and 46.2 MHz together with results of $LaPt_3Si$ that are consistent with a Korringa law with $1/T_1T = 12.34\ \mathrm{sec}^{-1}\,\mathrm{K}^{-1}$ in the T range measured. Apparently, $1/T_1T$ in $CePt_3Si$ is enhanced upon cooling due to the development of $4f$ derived magnetic fluctuations. For temperatures above 10 K, $1/T_1T$ appears to be field independent, whereas below this characteristic

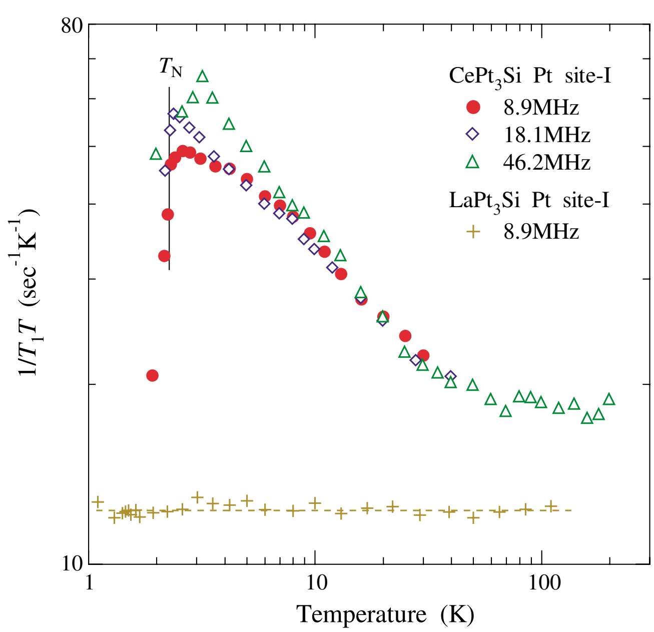

FIG. 2 (color online). The T dependence of $1/T_1T$ at site I at $f = 8.9$ (circles), 18.1 (squares), and 46.2 MHz (triangles) for $CePt_3Si$ together with the result of $LaPt_3Si$ (crosses). A dashed line shows a Korringa law with $1/T_1T = 12.34\ \mathrm{sec}^{-1}\,\mathrm{K}^{-1}$ for $LaPt_3Si$ in the measured T range.

temperature a significant H dependence is deduced. This temperature coincides roughly with the CEF level energy $\Delta E_1 \sim 16$ K. Corresponding to this, the $1/T_1T$ at $f = 8.9$ MHz seems to saturate below 10 K, whereas, at $f = 46.2$ MHz, $1/T_1T$ exhibits a sharp cusp at $T \sim 3$ K. These results suggest that the low-lying CEF level makes the relaxation behavior at low T dependent on H. Furthermore, the fact that $1/T_1T$ starts to decrease rapidly below T_N assures the onset of AFM order, consistent with the specific-heat result. Unfortunately, since the broadening in the spectrum below T_N makes it difficult to separately measure the spectrum at sites I and II, $1/T_1$ cannot be measured below T_N at site I.

Instead, the T dependencies of $1/T_1T$ at site II for $CePt_3Si$ and $LaPt_3Si$ are presented in a wide T range in Fig. 3, where the Korringa law $1/T_1T = 17.03\ \mathrm{sec}^{-1}\,\mathrm{K}^{-1}$ is valid at site II as well as at site I of $LaPt_3Si$. A difference in $1/T_1T$ is evident at sites I and II for $CePt_3Si$. In contrast to the result at site I, the $1/T_1T$ at site II shows a shallow peak around 6 K at $H \sim 1$ T (8.9 MHz) and stays constantly below $\sim$8 K at $H \sim 5$ T (46.2 MHz). The latter result is consistent with the $4f$ derived HF state, because the value of $1/T_1T$ is more strongly enhanced than the value in $LaPt_3Si$ as observed in either Ce or U-based HF compounds. This H dependence of $1/T_1T$ observed at site II originates from the low-lying CEF level as was already observed for site I. It is assumed that the reduction in $1/T_1T$ observed at low values of $H \sim 1$ and 2 T is also caused by the low-lying CEF level. This result contrasts

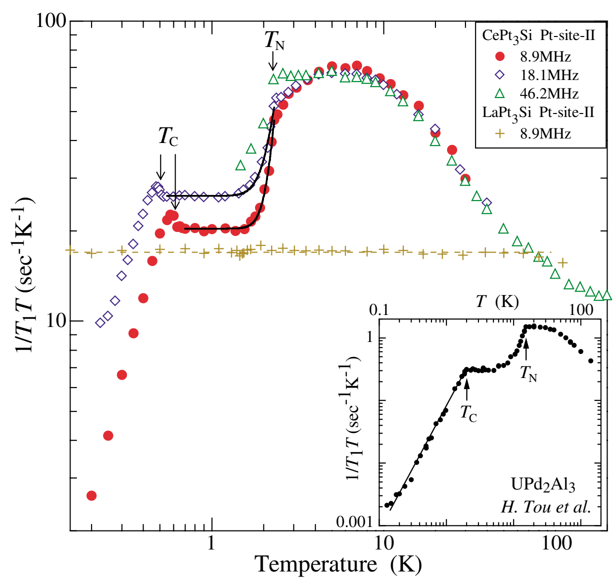

FIG. 3 (color online). The T dependence of $1/T_1T$ at site II for $CePt_3Si$ at $f = 8.9$ (circles), 18.1 (squares), and 46.2 MHz (triangles) together with the result of $LaPt_3Si$ (crosses). The dashed line shows a Korringa law with $1/T_1T = 17.03\ \mathrm{sec}^{-1}\,\mathrm{K}^{-1}$. The solid lines are least-square fits to the data below T_N using Eq. (1). The inset presents the T dependence of $1/T_1T$ of ^{27}Al for the antiferromagnetic HF superconductor UPd_2Al_3 with $T_N = 14.5$ K and $T_c = 2$ K [10].

with conventional Ce-based HF compounds where any well defined low-lying CEF level does not survive at low T. We point out that a similar T dependence of $1/T_1T$ was recently reported for the Pr-based HF superconductor $PrOs_4Sb_{12}$, although the low-lying CEF level is a non-Kramers doublet, yielding a broad peak around 3.5 K [11].

The T dependence of $1/T_1T$ undergoes a drastic decrease below $T_N = 2.2$ K without any critical divergence associated with the onset of AFM order as shown in Fig. 3. $1/T_1T$ below T_N is well reproduced by the following formula:

$$\frac{1}{T_1T} = A\exp\left(-\frac{\Delta}{k_BT}\right) + C \qquad (1)$$

as indicated by the solid lines in Fig. 3 for $f = 8.9$ and 18.1 MHz. Note that a $T_1T =$ const behavior is found for T well below T_N. The exponential decrease of $1/T_1T$ below T_N may be associated with a *gap* formed partially in the low-lying magnetic excitation spectrum. The respective values of energy gap Δ/k_B are estimated to be 23.3 and 16.8 K at $f = 8.9$ and 18.1 MHz. The size of gap is reduced by applying magnetic fields. The parameter C of Eq. (1) corresponds to the quasiparticle contribution. The respective values of $1/T_1T$ are about 20.3 and 26.2 $\mathrm{sec}^{-1}\,\mathrm{K}^{-1}$ at $f = 8.9$ and 18.1 MHz, being larger than $1/T_1T = 17.03$ in $LaPt_3Si$. This evidences that low-lying magnetic excitations are gapped, but low-lying quasiparticle excitations are rather in a gapless regime, giving rise to the $T_1T =$ const law even under the background of AFM order. As the gap size is reduced with increasing H, the value of $1/T_1T$ increases, indicative of a H induced transfer of low-energy spectral weight of quasiparticles. The present experiment also clarifies the vital role of the $4f$ derived CEF effect in forming a HF state at low T that is realized by virtue of the existence of a gap in the magnetic excitations in the AFM state. Thus, the SC transition emerges behind this unique HF state which coexists with the AFM phase.

In the SC state, the relaxation behavior of $CePt_3Si$ is quite different from that observed in unconventional Ce or U-based HF superconductors reported so far (see Fig. 3). Most HF superconductors display a T^3 power-law behavior that is consistent with a line-node gap below T_c without a coherence peak characteristic for conventional BCS superconductors [12–18,10]. As a typical example, the inset in Fig. 3 presents the T dependence of $1/T_1T$ for the AFM HF superconductor UPd_2Al_3 that undergoes the AFM and SC transitions at $T_N = 14.5$ K and $T_c = 2$ K, respectively [10]. By contrast, it is unexpected that $1/T_1T$ in $CePt_3Si$ exhibits a small peak just below T_c. However, the observed peak in $1/T_1T$ is much smaller than that observed for conventional BCS superconductors. In order to examine the H dependence of the relaxation behavior below T_c, the normalized value of $(1/T_1T)_{SC}/(1/T_1T)_N$ is plotted as a function of T/T_c at 8.9 MHz ($H \sim 1$ T) and 18.1 MHz ($H \sim 2$ T) as shown in Fig. 4. Here $(1/T_1T)_N$ corresponds to the values at the

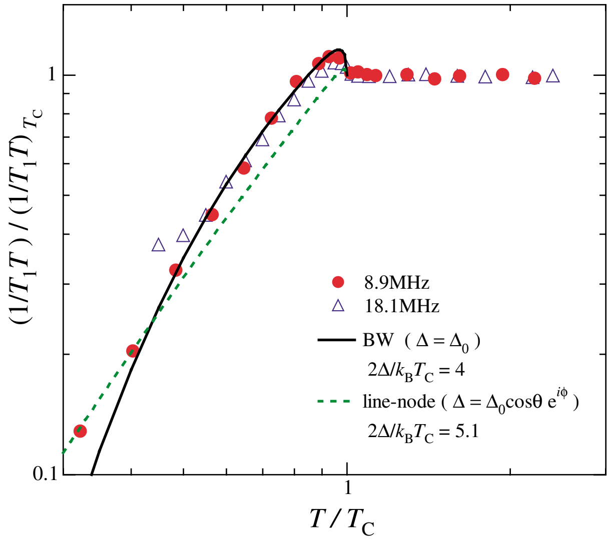

FIG. 4 (color online). The plot of $(1/T_1T)_{SC}/(1/T_1T)_N$ vs T/T_c at 8.9 (circles) and 18.1 MHz (triangles). Here $(1/T_1T)_N$ corresponds to the value at the normal state at 8.9 ($H \sim 1$ T) and 18.1 MHz ($H \sim 2$ T). The solid line is a tentative fit calculated by applying the Balian-Werthamer model (BW isotropic triplet SC state) with a value of $2\Delta/k_BT_c = 4$ [19]. The dashed line indicates a fit by a line-node gap model with $2\Delta/k_BT_c = 5.1$.

normal state at 8.9 MHz ($H \sim 1$ T) and 18.1 MHz ($H \sim 2$ T). Apparently, the peak in $(1/T_1T)_{SC}/(1/T_1T)_N$ is almost independent of H. $(1/T_1T)$ at $H \sim 2$ T seems to saturate at low T. Actually, the recovery curve of nuclear magnetization that depends on H suggests that the relaxation process is primarily dominated by the presence of vortex cores introducing the normal-state region. By contrast, $1/T_1T$ at 8.9 MHz ($H \sim 1$ T) continues to decrease down to $T = 0.2$ K, the lowest temperature measured. Neither an exponential law nor T^3 behavior is observed as far as the data down to $T = 0.2$ K are concerned. $CePt_3Si$ is the first HF superconductor that exhibits a peak in $1/T_1T$ just below T_c and, moreover, does not follow the T^3 law reported for most of the unconventional HF superconductors.

In order to inspect the overall relaxation behavior of noncentrosymmetric $CePt_3Si$ below T_c, a tentative SC model was tried by applying the Balian-Werthamer model (BW isotropic spin-triplet SC state, solid line in Fig. 4) with a value of $2\Delta/k_BT_c = 4$ [19]. Note that the peak in $1/T_1T$ would indicate the presence of an isotropic energy gap, even though the *coherence effect,* inherent to the isotropic spin-singlet *s*-wave pairing state, is absent. Moreover, $1/T_1T$ does not follow a simple power-law behavior, indicating a line-node gap at the Fermi surface (dashed line, Fig. 4). It is interesting to note that the BW model describes fairly well the data just below T_c. In order to conclude a more detailed structure of SC energy gap from the $1/T_1$ measurements, however, the experiment at further low temperatures and fields is required. In the new HF compound $CePt_3Si$, however, an inversion center is absent in its crystal symmetry. Therefore, the novel relaxation behavior found below T_c may justify the possible existence of some kind of a new SC state being realized in the noncentrosymmetric $CePt_3Si$.

In conclusion, the present ^{195}Pt-NMR study on $CePt_3Si$ has clarified novel electronic and magnetic properties in the PM and AFM states and a relevant new class of a HF SC state. The CEF energy separation of the low-lying level is as small as $\Delta E_1 \sim 10$–16 K, consistent with neutron results. A HF state is realized for temperatures below $\sim$6 K. The magnetic excitation spectrum has a gap that depends on the magnetic field. The HF quasiparticles remain in a gapless regime in the T region well below T_N, giving rise to a $T_1T =$ const behavior. The application of magnetic fields causes a reduction in size of the magnetic gap and simultaneously the increase in spectral weight of quasiparticles at the Fermi level, having some relevance with the presence of low-lying CEF levels. The Pt-T_1 measurements have probed the coexistence of AFM and SC orders on the microscopic level. $CePt_3Si$ is the first HF superconductor that reveals a peak in $1/T_1T$ just below T_c and, additionally, does not follow the T^3 law reported for most unconventional HF superconductors. Thus, the novel relaxation behavior found below T_c sheds light on the possibility of a new class of a SC state being realized in noncentrosymmetric $CePt_3Si$. The experimental findings presented in this work deserve future theoretical studies to unravel the SC OP symmetry for the noncentrosymmetric compounds in general.

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