NMR Study of Heavy Fermion Superconductor with No Inversion Symmetry CePt₃Si

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We report ¹⁹⁵Pt and ²⁹Si NMR studies of an antiferromagnetic heavy fermion superconductor CePt₃Si with no inversion symmetry in the crystal structure. The temperature dependence of spinlattice relaxation rates $(1/T_1)$ for Pt and Si nuclei measured between 2 K and 300 K might be explained by the contributions from a low-lying Crystalline-Electric-Field level and a quasiparticle due to a hybridization between the ground state and conduction electrons. Just below the superconducting transition temperature (T_c) no remarkable enhancement in $1/T_1$ was observed within an experimental error. No significant decrease of ²⁹Si Knight shift was observed for parallel direction to the *c*-axis below T_c . This indicates that spin triplet pairing is probably realized for the superconductivity.

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I. INTRODUCTION

Last year, Bauer *et al.* reported a new heavy fermion superconductor CePt₃Si with a Néel temperature (T_N) and a superconducting (SC'ing) transition temperature (T_c) of 2.2 K and 0.75 K, respectively.[1] The superconductivity (SC) in this compound is realized in the longrange antiferromagnetic (AF) state, which is in contrast with SC in the previous Ce-based compounds where SC occurs in the nonmagnetic or AF spin-fluctuating state.

The first feature of this superconductor is no spatial inversion symmetry along the *c*-axis in the unit cell, which generally favors spin singlet pairing in the SC. The second feature is the large dH_c/dT (= -8.5 T/K) and H_{c2} (~5 T), which suggest that Cooper pairs are formed in the heavy quasi-particle state. The large H_{c2} , which exceeds the Pauli-Clogston limiting field estimated from the T_c , might be a sign of spin triplet pairing. A mixed state with spin singlet and triplet pairings might also be one of the explanations to this paradox.[2]

To investigate the electronic state of this compound microscopically, we performed 195 Pt and 29 Si NMR experiments on polycrystalline CePt₃Si samples.

II. EXPERIMENT

The starting materials of samples are Ce, Pt, and Si with 99.9%(3N), 99.95%(3N5), and 6N purity, respectively. Polycrystalline samples were prepared from stoichiometric amounts of starting materials by arc melting in Ar atmosphere. Successively, the ingots were annealed at 950°C for one week. The powder X-ray diffraction measurement showed no extra phase. A conventional pulsed spectrometer and a SC'ing magnet were employed for NMR measurements.

III. RESULT AND DISCUSSION

There exist crystallographically two inequivalent Pt sites in $CePt_3Si$: one is a Pt(1) site which is located near the face center position of the *ac*-plane in the unit cell,



FIG. 1: Line shapes of Pt and Si NMR measured at 4.2 K in $CePt_3Si$ powder, which was partially aligned its *c*-axis along an applied magnetic field.

the other site Pt(2) is on the *c*-axis together with the Si site.[1] The site occupancy-ratio for Pt(1) and Pt(2) is 2:1. Under an applied magnetic field, due to anisotropic susceptibilities, some mechanical vibrations in the powder can easily make the crystal axis in the microcrystals of CePt₃Si orient to the magnetically-easy axis. Shown in Fig. 1 are the NMR spectra of ¹⁹⁵Pt and ²⁹Si for an aligned $(H \parallel c$ -axis) microcrystal of CePt₃Si at 4.2 K obtained by sweeping the external field at a constant frequency of 41 MHz. The reason the intensity ratio of two Pt spectra is not exactly two may be due to an imperfect alignment of the crystal axis under the applied field. The Si spectrum, however, has a narrow line width, even in randomly oriented powder, and only a slight decrease of the line width was observed after the alignment. This narrow width is partly the result of a weak coupling between s(p) electrons in Si and 4f magnetic moment of Ce.

According to the neutron scattering experiment in the AF state, Ce 4f magnetic moments of ~0.16 $\mu_{\rm B}$ align ferromagnetically in the c-plane, and stack antiferromagnetically along the c-axis.[3] Below $T_{\rm N}$, line widths for all the spectra actually start to increase, due to an appearance of an internal field coming from the AF magnetic ordering (not shown in Fig. 1). Indeed, NMR spectra from two Pt sites overlap each other below $T_{\rm N}$. Thus, it



FIG. 2: Temperature dependence of Knight shift for Si around $T_{\rm c}$. The dotted line represents a temperature independent term of K (K_0 =0.11%).

becomes difficult to measure T_1 for each site precisely, as described later.

The Knight shift (K) measurement was performed to obtain the hyperfine coupling constant $(A_{\rm hf})$ at each site and the temperature (T) independent term of K, which is necessary to evaluate K below T_c . A magnetic field was calibrated with an NMR signal of Pb metal (γ =8.874 MHz/T, K=1.46%), because the gyromagnetic ratio of Pb is between Pt ($\gamma = 9.094 \text{ MHz/T}$) and Si (8.4577 MHz/T). From a linear fit to the data, which is the K plotted against the susceptibility (χ) with T as an implicit parameter, $A_{\rm hf}$'s for the Pt(1), the Pt(2), and the Si sites parallel to the *c*-axis are evaluated as +2.99, +7.80, and +1.46 kOe/ $\mu_{\rm B}$, respectively. The $A_{\rm hf}$ value of Si in this compound is close to those of URu₂Si₂ (+3.6 kOe/ $\mu_{\rm B}$), CePd₂Si₂(+2.84 kOe/ $\mu_{\rm B}$), and $\text{CeRh}_2\text{Si}_2(+2.34 \text{ kOe}/\mu_B)$.[5, 6] This is partly due to weak hybridization between s(p) electrons in Si and f(s) electrons in Ce, irrespective of the magnetic property of each specimen.

Here, in the paramagnetic state, K was measured at a peak position of the spectrum for H||c case and the data of χ for the H||c axis are taken from [4], because our measured χ 's for polycrystalline samples were not available. The *T*-independent K, which is coming mainly from the Van Vleck orbital term and the diamagnetic contributions on each site, is obtained experimentally as an intercept on the K axis, which corresponds to the extrapolation of the $K-\chi$ line to high *T*. The *c*-axis of microcrystals was aligned along the magnetic field direction (H||c). From the $K-\chi$ line the residual shift, K_0 , of Si is estimated as +0.11% for this sample.

To obtain the information on the spin state of SC'ing pair electrons, we measured the *T*-dependence of *K* of Si around T_c at 13 MHz (1.537 T). The observed Knight shift is, generally, expressed as $K = K_s(T) + K_0$. Here, $K_s(T)$ and K_0 are arising from the *T*-dependent spin susceptibility and the *T*-independent term, respectively. The latter is about +0.11%, as mentioned before. The former term is, of course, essential for determining the parity of Cooper pairs. Shown in Fig. 2 is the *T*dependence of the peak position of Si NMR spectrum for



FIG. 3: Temperature dependence of $1/T_1$ for Pt(1), Pt(2), and Si. The behavior of non-magnetic LaPt₃Si is also shown with dashed lines. Below T_c , "2exp-short" and "2exp-long" mean the data of short relaxation-time and long relaxationtime components deduced from the total relaxation by a two component fit, respectively.

H||c. No significant shift was observed between $T_{\rm c}(H)$ and 0.3 K, as can be seen in this figure. This result suggests that spin triplet pairing is probably realized for SC.

Then, the spin-lattice relaxation rates $(1/T_1)$ were measured at the peak-positions for $H \parallel c$ axis. Since ¹⁹⁵Pt and ²⁹Si nuclei have nuclear spins of I=1/2, the nuclear relaxation 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 magnetizations for the thermal equilibrium condition at a time t after the saturation pulse(comb-pulse), respectively. $1/T_1$ is uniquely determined by a single component above T_c . Fig. 3 shows the T-dependence of $1/T_1$ of the Pt(1), the Pt(2) and the Si sites. As seen in this figure, our sample shows almost the same T-dependence in $1/T_1$ for these sites. To elucidate a contribution from the Ce magnetic moment, nonmagnetic LaPt₃Si was also measured. Its T-dependence shows a typical metallic behavior $(1/T_1 \propto T)$ indicated by dashed lines. As is well known, a magnetic contribution from a Ce^{3+} moment in $CePt_3Si$ makes the relaxation rate larger than that in LaPt₃Si in almost the whole T-range. An enhancement in $1/T_1$ around 10 K may be explained with a first excitation level ($\Delta=12$ K) of Crystalline-Electric-Field (CEF) measured by the recent neutron scattering experiment. [3] To understand the Tevolutions in $1/T_1$ for the Pt(1), the Pt(2) and the Si sites consistently, the form factors, including an anisotropic hyperfine coupling constant and geometric factors, must be taken into account, besides the CEF effect. This is an important future problem.

Near the AF transition, $(1/T_1)$'s are slightly enhanced with no distinct peak, suggesting the system does not show any critical slowing-down of fluctuations of the Ce moment. Below T_N , $(1/T_1)$'s decreased rapidly due to a formation of an AF gap at the Fermi surface. On cooling



FIG. 4: Temperature dependence of $1/T_1$ for Si through T_c . The dashed lines are guides for eyes for exponential behaviors in isotropic SC'ing gaps.

it is difficult to measure the $(1/T_1)$'s of Pt(1) and Pt(2) separately, owing to the overlapping for the spectra of Pt(1) and Pt(2). Therefore, just the *T*-dependence of $1/T_1$ for Pt(1), where AF fluctuations are almost canceled crystallographically and a sharp line width from Pt(1) could be found in a widely spread line shape, was measured. In the normal state far below T_N , $1/T_1$ becomes proportional to *T*, which means that the system is in the Fermi liquid state.

To get the information of the SC'ing energy gap, we carried out two types of $1/T_1$ measurements: (1) an ordinary comb-pulse method for the Pt(1) and the Si sites and (2) a field cycling method for the Si site. T_c under an applied field of 1.69 T for NMR was found to be 0.55 K by using ac χ , which is very close to the data of Bauer *et al.*[1]

As is well known, type-II superconductors under an applied field in the SC'ing state are in a vortex state. When a sample has comparable SC'ing coherence length $(\xi(T))$ with a distance between vortices, the influence of the vortex core to nuclear relaxation is not negligible. Thus, two components, in general, appear in T_1 below T_c : a short relaxation time component arising from the presence of the vortex core induced by applying a magnetic field and a long component attributed to an intrinsic relaxation in the SC'ing region. In this way, we evaluated only a long relaxation component deduced from the total nuclear relaxation by a two component fit. As described before, Si atoms crystallographically occupy just one site in the crystal structure. The NMR spectrum at the Si

site has narrower line width with weaker intensity than that at Pt, which favors T_1 measurement of Si, because there may exist a spin diffusion effect which causes extrinsic rapid relaxation in the wide Pt spectrum. Due to these disadvantageous factors, sufficient accuracy for T_1 measurement on Pt was not expected. As seen in Fig. 3, $(1/T_1)$'s for the Pt and the Si in the SC'ing state overall show similar behaviors, contrary to our expectation. Moreover, no remarkable Hebel-Slichter coherence peak for either nuclei was observed just below T_c . Further below T_c , $1/T_1$ drastically decreases with decreasing T. Assuming the SC'ing gap is isotropic, the value of the SC'ing gap is roughly estimated to be about $2\Delta = 3 \sim 5k_BT_c$.

Next, to evaluate the long relaxation time of the Si, we tried to measure it by the field cycling method, which makes an NMR relaxation measurement under zero external field possible. The obtained results were shown by open squares in Fig. 4, together with $1/T_1$ for Si shown in Fig. 3. The SC'ing energy gap, 2Δ , was estimated to be about $5k_{\rm B}T_{\rm c}$, assuming an isotropic energy gap. Further experiments are now in progress.

IV. SUMMARY

The present NMR results suggest that the SC'ing state coexists microscopically with the AF ordered state. Through $T_{\rm c}$, K for the Si site showed no significant change. This result means that the SC is probably in a spin-triplet state. Secondly, we measured $1/T_1$ and K for the Pt(1), the Pt(2), and the Si sites of $CePt_3Si$ in the wide T-range. In the paramagnetic state, the Tbehavior of $1/T_1$ may be explained mainly by CEF excited levels. Below $T_{\rm N}$, $1/T_1$ decreased rapidly due to the formation of an energy gap associated with the AF ordering. Above $T_{\rm c}$, the system is in the Fermi-liquid state. Below T_c , $1/T_1$ drastically becomes smaller due to the superconducting energy gap, which is estimated to be about $3 \sim 5k_{\rm B}T_{\rm c}$. The detailed T_1 measurements below $T_{\rm c}$ regarding the structure of the SC'ing gap with nodal points or lines are now in progress.

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