Two superconducting phases in CePt$_3$Si confirmed by NMR

Koh-ichi Ueda, Gaku Motoyama and Takao Kohara
Graduate School of Material Science, University of Hyogo, Kamigori-cho, Ako-gun, Hyogo
678-1297, Japan
E-mail: ueda@sci.u-hyogo.ac.jp

Abstract. Recent specific heat experiments in CePt$_3$Si of good quality gave an evidence of coexistence of two phases, which have distinct $T_c$ and $T_N$ for each phase. NMR spectrum of $^{29}$Si also showed a complicated line shape due to a co-existence of two phases below $T_N$. One phase is an ordinary AF state and the other is a paramagnetic like phase, in which the internal field is somewhat small. The AF internal field deduced by NMR is expected to be parallel to the $c$-axis at Si site. With decreasing temperature below $T_c$, $1/T_1$ measured at the satellite peak decreased rapidly followed by $T^3$ with no enhancement just below $T_c$.

1. Introduction
Several interesting superconductors (CePt$_3$Si, CeIrSi$_3$, LiPt$_3$B$_2$ etc.) with non-centrosymmetry in their crystal structures have recently been reported by many groups in the world. The spin state in these superconductors attracts many scientists’ interests due to a lack of inverse symmetry in the crystal structure. So, several NMR experiments, which focused on the temperature dependence of relaxation rate and Knight shift through superconducting transition temperature ($T_c$), were especially reported for CePt$_3$Si with Néel temperature ($T_N$) and $T_c$ of 2.2 K and 0.75 K, respectively [1, 2]. Superconductivity in this compound is realized in the long-range antiferromagnetic state. Despite of many published papers, some unsolved problems of the magnetic and superconducting (SC) behaviors still remain. These may correspond to a small deviation from stoichiometry and/or an annealing condition on the prepared samples. In this paper, we report the recent results obtained by NMR and specific heat experiments.

2. Experimental
Polycrystalline CePt$_3$Si samples were prepared by arc melting in Ar atmosphere from the amounts of constituent elements Ce, Pt, Si and $^{29}$Si with purity of 3N, 3N5, 6N and 3N8 (99.8% enriched), respectively. The annealing temperature was 950°C for 1 week and lowered to room temperature over 3 days. For NMR measurement the annealed CePt$_3$Si with enriched $^{29}$Si was used, which was prepared independently. For the specific heat measurement both heat-treated and non heat-treated samples were prepared. Hereafter, heat-treated and non heat-treated samples are labeled as “annealed” and “as cast”, respectively. X-ray diffraction patterns for all the samples indicated no extra phase. Specific heat was measured using an adiabatic heat pulse method. A conventional pulsed spectrometer and SC magnet were employed for NMR measurements.
Figure 1. Temperature dependence of the specific heat in the form of $C/T$ of CePt$_3$Si. Circles and triangles show the data of “annealed” sample and “as cast” sample, respectively. $T_{cL}$ and $T_{cH}$ stand for $T_c$’s in “low $T_c$ phase” and “high $T_c$ phase”, respectively.

Figure 2. NMR spectra of $^{29}$Si nuclei obtained under different sample condition in CePt$_3$Si at 1.3 K. (a) A spectrum of the powder sample ($c$-axis∥magnetic field). (b) A spectrum of the powder sample (non aligned to magnetic field).

3. Results and Discussion

In our recent specific heat experiments, the well “annealed” Ce$_{1.01}$Pt$_3$Si sample exhibited a sharp and steep jump at 0.5 K for SC transition and a clear and large jump at 2.2 K corresponding to an antiferromagnetic (AF) transition, as displayed in Fig. 1.[3] On the other hand, “as cast” CePt$_3$Si sample showed a broad peak of SC transition at 0.75 K and a broad and low bump corresponding AF transition around 1.5 to 3 K. The latter peak in “as cast” may be ascribed to a distribution of $T_N$ and/or internal magnetic field. In other samples except for “annealed” and “as cast”, an intermediate value of $T_c$ between 0.5 K and 0.75 K was not observed, but only two distinct $T_c$ of 0.5 K and 0.75 K were seen. These results remind us high possibility of coexistence of two phases, which are composed of an AF lower $T_c$ phase and a paramagnetic like higher $T_c$ phase with low internal field. Hereafter, the former and the latter phases are referred to as “low $T_c$ phase” and “high $T_c$ phase”, respectively. As mentioned above, “low $T_c$ phase” with $T_N$ of 2.2 K and $T_c$ of 0.5 K seems to be an intrinsic phase of CePt$_3$Si, because it was also found in a well “annealed” sample and a single crystal.[3, 4] To the contrary, “high $T_c$ phase” is considered as a parasitic or an accompanying phase produced by an imperfection and/or a disorder of atomic arrangement, since this phase appears in the sample prepared by non heat-treatment.

Thus, in order to get the magnetically ordered state for each phase in more detail the field-swept NMR were performed by changing the field direction and the temperature. Under an applied magnetic field, due to anisotropic susceptibilities, some mechanical vibrations in the powder can easily make the crystal axis in microcrystals of CePt$_3$Si orient to the magnetoically-easy axis. In the case of CePt$_3$Si, the $c$-axis is the magnetically-easy axis for all temperature range [5]. Fig. 2(a) shows the NMR spectrum of $^{29}$Si for aligned ($H$∥$c$-axis) micro-crystals of the “annealed” sample. Needless to say, below $T_N$ the line width is considered to be broaden by the internal field ($H_{int}$) due to AF ordering. According to the neutron diffraction study in the AF state, Ce 4$f$ magnetic moments of 0.16µB align ferromagnetically in the $c$-plane and stack antiferromagnetically along the $c$-axis deduced from the (1, 0, 1/2) and (0, 0, 1/2) reflections.[6]

Now, an effective field ($H_{eff}$) at constituent nuclei can be approximately expressed as
Figure 3. Temperature dependence of relaxation rate of $^{29}$Si NMR. The marks of $\bullet$ and $\circ$ show the relaxation rates of “low $T_c$ phase” and “high $T_c$ phase”, respectively.

$H_{\text{eff}} = H_0 + H_{\text{int}} \cdot \cos \theta$ for $H_{\text{int}} \ll H_0$, where $H_0$ and $\theta$ are an external field and an angle between $H_0$ and $H_{\text{int}}$, respectively. As is well known, the observed NMR spectrum is expected to have a rectangular or a trapezoidal shape for randomly aligned powders against a magnetic field in the AF state.[7] However, contrary to our expectation, the field swept NMR spectrum with completely different shape was observed in unoriented sample fixed by methyl alcohol, as displayed in Fig. 2(b). In order to discuss this discrepancy precisely, the angle evolution of NMR spectrum between the directions of an aligned axis and an applied field is performed. The peaks at both ends of the spectrum move toward the center of spectrum with increasing an angle from the $c$-axis. To explain the angle evolution of peaks of the oriented sample, the direction of internal magnetic field must be parallel to the $c$-axis at Si site. In NMR experiments above 0.4 T, this assignment regarding the direction is opposite to those of the published papers.[2, 8] Recent neutron scattering experiments showed that the AF reflection intensity at (0, 0, 1/2) increases markedly above 2 T.[4, 9]. The shift at the peak position is estimated as about $6 \times 10^{-4}$ T to lower field to keep a resonance field under the experimental condition ($H_0=1.2$ T, $H_{\text{int}}=0.024$ T). No remarkable shift of a central peak, however, was observed below $T_N$ (not shown in the figure). This suggests that small or nearly zero internal field appears at Si sites in “high $T_c$ phase”.

Next, we propose the origin regarding the line width as follows. The widely spread rectangular spectrum and the central peak without any shift in the AF state are considered to come mainly from “low $T_c$ phase” and “high $T_c$ phase”, respectively. The central spectra observed around 1.238 T, of course, are composed of two signals coming from “low $T_c$ phase” and “high $T_c$ phase”. The whole intensity ratio of the former to the latter is estimated to be around two to one. As a result, the values of $T_N$ and the internal magnetic field have widely been distributed and partially extended to zero. The low internal field appeared in the paramagnetic like region may be due
to a partial improvement of centrosymmetry in the crystal structure.

Now, the relaxation rates were measured at the central peak (■) and satellite peaks (▲) in Fig. 2(a). The recovery behavior at the satellite peak (▲) was described by one relaxation time, indicating that the satellite signal comes from one phase. As a matter of fact, the recovery at the central peak (■) was found to contain at least two relaxation components, which suggests that the central signal is from two phases, as mentioned before. Above $T_N$, as two kinds of signals are overlapping together, the relaxation time was estimated from two-exponential fitting in the whole nuclear magnetization recovery assuming that the component ratio of “high $T_c$ phase” was one third. This is quite reasonable from the point of the signal intensity ratio, as mentioned above. Fig. 3 shows the temperature dependence of $1/T_1$ on “high $T_c$ phase” and “low $T_c$ phase” marked by □ and ●, respectively. The values of $T_N$ and $T_c$ for each phase show those deduced from the specific heat measurement, as mentioned in the former part. As seen in this figure, $1/T_1$ for “low $T_c$ phase” decreases drastically below $T_N$ with a sudden drop at $T_N$, which is associated with a large jump at $T_N$ in the results of specific heat. This result suggests the formation of antiferromagnetic energy gap upon cooling below $T_N$. On the other hand, $1/T_1$ for “high $T_c$ phase” has a distribution of $T_N$ around 2 K, which also qualitatively agrees with the results of specific heat measurements. Below $T_c$, $1/T_1$ measured at satellite peaks has two components, which are from the vortex core and the superconducting regions. They were shown by ● and ■ in Fig. 3, respectively. As shown in this figure, no enhancement of $1/T_1$ was seen just below $T_c$ and decreased rapidly followed by $T^3$-law down to 0.12 K. On the other hand, $1/T_1$ deduced from the vortex core keeps $T_1 T = \text{const}$. Needless to say, the relaxation behavior at the central peak were too complicate to analyze precisely, because it has four components for the nuclear relaxation: “high $T_c$ phase” has superconducting and vortex regions and so does “low $T_c$ phase”.

In conclusion, we could measure the $1/T_1$ of $^{29}$Si for two phases of annealed CePt$_3$Si sample corresponding to the “low $T_c$” and “high $T_c$” phases, respectively. An existence of two superconducting phases in CePt$_3$Si proposed by the recent specific heat measurement was confirmed microscopically by the spectra and the nuclear relaxation rate of NMR. With decreasing temperature below $T_c$, $1/T_1$ measured at the satellite peak decreased rapidly followed by $T^3$ with no enhancement just below $T_c$. On the contrary, the NMR spectrum of $^{29}$Si could not simply be explained by the arrangement of magnetic moment obtained by the neutron diffraction. A modified structure, in which magnetic moments are parallel to the $c$-axis, is favorable to understanding of the spectrum. To get a detailed electronic state for each phase by NMR, the improved sample, which has almost all of “high $T_c$ phase” or “low $T_c$ phase” with enriched $^{29}$Si, is highly desired.

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