Two superconducting phases in $CePt_3Si$ confirmed by NMR

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Abstract. Recent specific heat experiments in $CePt_3Si$ 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 lineshape 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. The temperature evolution of relaxation times for two phases are qualitatively consistent with the results of specific heat measurements.

1. Introduction

Several interesting superconductors ($CePt_3Si$, $CeIrSi_3$, $LiPt_3B_2$ 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 $CePt_3Si$ 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 $CePt_3Si$ 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 $CePt_3Si$ 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 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.

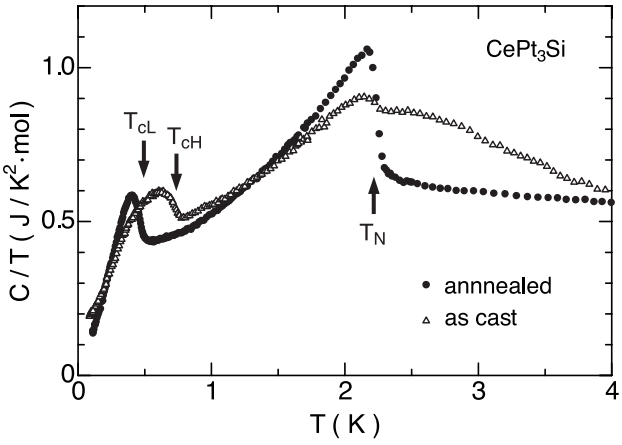

Figure 1. Temperature dependence of the specific heat in the form of C/T of $CePt_3Si$. Circles and triangles show the data of "annealed" sample and "as cast" sample, respectively. T_{cL} and T_{cH} denote T_c's in "low T_c phase" and "high T_c phase", respectively. (see text)

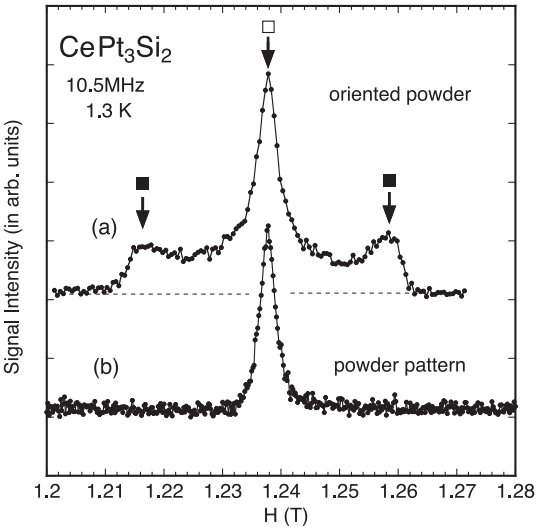

Figure 2. NMR spectra of ^{29}Si nuclei obtained under different sample condition in $CePt_3Si$ at 1.3 K. (a) A spectrum of the powder sample (c-axis$\|$magnetic field). (b) A spectrum of the powder sample (non aligned to magnetic field).

3. Results and Discussion

In our recent specific heat experiments, the well "annealed" $Ce_{1.01}Pt_3Si$ 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" $CePt_3Si$ 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 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 phase and a paramagnetic like phase with low internal field. Hereafter, the AF lower T_c and the paramagnetic like higher T_c 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 $CePt_3Si$, because it was 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 electronic state for each phase in more detail by NMR, the information regarding the directions of the external field and the crystalline axis for powdered sample is highly desired. Under an applied magnetic field, due to anisotropic susceptibilities, some mechanical vibrations in the powder can easily make the crystal axis in microcrystals of $CePt_3Si$ orient to the magnetically-easy axis. In the case of $CePt_3Si$, 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 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 $4f$ magnetic moments of $0.16\mu_B$ align ferromagnetically in the c-plane and stack antiferromagnetically along the c-axis deduced from

an observation of (1, 0, 1/2) and (0, 0, 1/2) reflection.[6]

Now, an effective field ($H_{\rm eff}$) at constituent nuclei can be approximately expressed as $H_{\rm eff} = H_0 + H_{\rm int} \cdot \cos\theta$ for $H_{\rm int} \ll H_0$, where H_0 and θ are an external field and an angle between H_0 and $H_{\rm int}$, 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. However, contrary to our expectation, the field swept NMR spectrum with completely different shape was observed in powdered sample fixed by methyl alcohol, as displayed in Fig. 2(b). As seen in the figure, a central peak is considered to come from non-aligned region by an applied magnetic field. In order to discuss this discrepancy precisely, the angular 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 evolution of peaks of the oriented sample, the direction of internal magnetic field must be parallel to the c-axis at Si site. At least above 0.4 T in NMR experiments, this assignment regarding the direction is opposite to those of the published papers.[2, 7] Recent neutron scattering experiments showed that the AF reflection intensity at (0, 0, 1/2) increase markedly above 2 T [4], which is different from other data of (0, 0, 1/2) reflection.[8]

The shift at the diverging point is estimated as about 6×10^{-4} T to lower field to keep a resonance field under the experimental condition (H_0=1.2 T, $H_{\rm int}$=0.024 T). No remarkable shift of a central peak, however, was observed below $T_{\rm N}$ (not shown in the figure). This means that small or nearly zero internal field appears at some parts of Si, which corresponds to a central peak in the spectrum.

This discrepancy of the line width cannot be well explained at present.

Namely, the widely spread rectangular spectrum and the central peak without any shift in the AF state are considered to come mainly from "low $T_{\rm c}$ phase" and "high $T_{\rm c}$ phase", respectively. The intensity ratio of the former to the latter is estimated to aout two to one. As a result, the values of $T_{\rm N}$ 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.

The relaxation behavior for each phase can be measured separately at the characteristic magnetic field in the NMR spectrum. Below $T_{\rm N}$, the relaxation rates ($1/T_1$) of "high $T_{\rm c}$ phase" and "low $T_{\rm c}$ phase" are measured at the central peak (□) and satellite peaks (■) in Fig. 2(a), respectively. 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. Above $T_{\rm N}$, as two kinds of signals are overlapping together, the relaxation time was estimated from two-exponential fitting of the nuclear magnetization recovery assuming that the component ratio of "high $T_{\rm c}$ 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 $T_{\rm c}$ phase" and "low $T_{\rm c}$ phase" marked by ○ and ● , respectively. The values of $T_{\rm N}$ and $T_{\rm c}$ for each $1/T_1$ show those deduced from the specific heat measurement, as mentioned in the former part. As seen in this figure, $1/T_1$ for "low $T_{\rm c}$ phase" decreases drastically below $T_{\rm N}$ with a sudden drop at $T_{\rm N}$, which is associated with a large jump at $T_{\rm N}$ in the results of specific heat. This result suggests the formation of antiferromagnetic energy gap upon cooling below $T_{\rm N}$. On the other hand, $1/T_1$ for "high $T_{\rm c}$ phase" has a distribution of $T_{\rm N}$ around 2 K, which also qualitatively agrees with the results of specific heat measurements. Both relaxations showed no superconducting transitions below $T_{\rm c}$'s down to 0.3 K, which is due to the lowering $T_{\rm c}$ under applied field.

In conclusion, we could measure the nuclear relaxation rates ($1/T_1$) of ^{29}Si for two phases of annealed $CePt_3Si$ sample corresponding to the "low $T_{\rm c}$" and "high $T_{\rm c}$" phases, respectively.

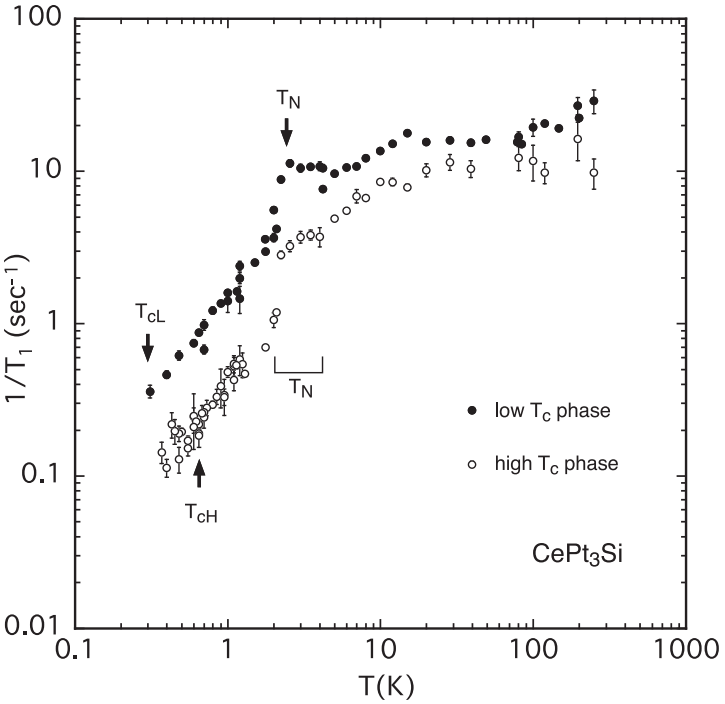

Figure 3. Temperature dependence of relaxation rate of ^{29}Si NMR. The marks of ● and ○ show relaxation rates of "low T_c phase" and "high T_c phase", respectively.

An existence of two superconducting phases in $CePt_3Si$ proposed by the recent specific heat measurement was confirmed microscopically by the spectra and the nuclear relaxation rate of NMR. Although the mechanism on difference of the line width in the spectrum is not clear at present, the ^{29}Si NMR spectrum explained a scenario of coexistence composed of two phases very well. 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 samples are highly desired. They have almost all of "high T_c phase" and "low T_c phase" with enriched ^{29}Si, which are quite similar to those for the specific heat measurement.

Acknowledgments

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