# Microscopic Properties In Non-Centrosymmetric Superconductors

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**Abstract.** Below $T_N$, the NMR spectrum of $^{29}Si$ in $CePt_3Si$ shows a rather narrow resonance line for the randomly oriented powder sample, while the oriented powder sample has a wide spectrum. To explain these spectra, a coexistence model composed of two phases was proposed. 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 is expected to be parallel to the *c*-axis at Si site. This result cannot be explained by the magnetic structure obtained by the neutron diffraction experiment.

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## INTRODUCTION

Several interesting superconductors ($CePt_3Si$, $KOs_2O_6$, $CeIrSi_3$, $LiPt_3B_2$ 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 their crystal structures. 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.

## 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. Hereafter, heat-treated and non heat-treated samples are labeled as "annealed" and "as cast", respectively. X-ray diffraction patterns indicated no extra phase for both samples. Specific heat was measured using an adiabatic heat pulse method. NMR experiments in the paper were performed on "annealed" $Ce_{1.01}Pt_3Si$ sample. On angular dependence of NMR signal under an applied

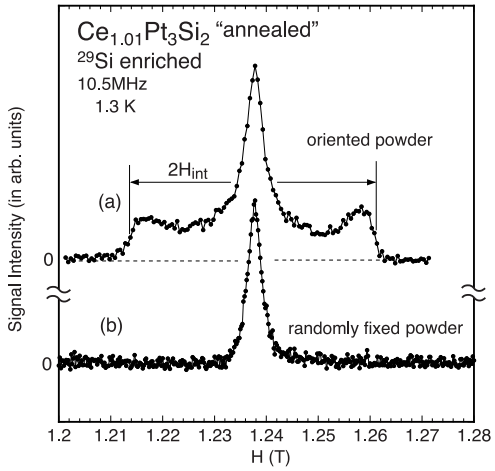


**FIGURE 1.** NMR spectra of $^{29}$Si nuclei obtained under different sample condition in "annealed" $Ce_{1.01}Pt_3Si$ at 1.3 K. (a) A spectrum of the powder sample (**H** // *c*-axis). The full line width corresponds to the internal field ($2H_{\rm int}$). (b) A spectrum of the powder sample (non aligned to magnetic field).

field: the NMR was measured under an external field rotated to change the angle between the directions of an aligned axis and an external magnetic field.

## RESULTS AND DISCUSSION

Under an applied magnetic field ($H$), 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 [3]. Fig. 1(a) shows the NMR spectrum of $^{29}$Si for aligned (**H** // $c$-axis) microcrystals of the sample. Needless to say, below $T_{\rm N}$ the line width is considered to be broaden by an internal field ($H_{\rm int}$) due to antiferromagnetic (AF) ordering. According to the neutron diffraction study in the AF state [4], Ce $4f$ magnetic moments of $0.16\mu_{\rm B}$ align ferromagnetically in the $c$-plane and stack antiferromagnetically along the $c$-axis.

As is well known, the observed NMR spectrum is expected to have a rectangular or a trapezoidal shape for randomly oriented powders against a magnetic field in the AF state for $H_{\rm int} \ll H_0$, where $H_0$ is an external field [5]. 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. 1(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 issue precisely, the angular evolution of NMR spectrum between the directions of an aligned axis and an applied field is performed. Fig. 2 shows the angular dependence of an external field in the spectrum against the $c$-axis at 1.3 K. As can be seen in this figure, 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. This assignment on direction is quite different from that of the

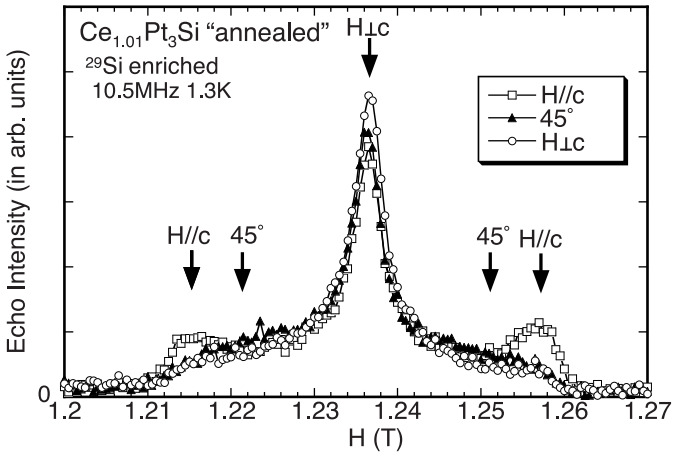


**FIGURE 2.** Spectra obtained by changing the angle between the oriented direction of the powder and an external field. Arrows indicate peak positions estimated from angles between $H_0$ and $H_{\rm int}$.

published paper [2, 6]. To confirm non-variation of the direction on the magnetically easy axis in the paramagnetic state and in the AF state, the sample was cooled down to 1.3 K under zero external field and then the NMR spectrum was measured under an applied field. No essential difference of the spectra was observed between the sample aligned at 4.2 K in the paramagnetic state and the sample at 1.3 K in the AF state (not shown in the figure).

The internal field parallel to the *c*-axis cannot be deduced from the magnetic structure proposed by the neutron scattering shown in Fig. 3(a). To make the internal field parallel to the *c*-axis, two kinds of magnetic structures are adopted as a candidate, as displayed in Fig. 3(b) and Fig. 3(c). In the magnetic structure of Fig. 3(b), the Pt(1) sites, which are crystallographically equivalent, however, should split into two magnetically inequivalent sites (Pt(1a) and Pt(1b) in Fig. 3(b)). Since the observed Pt NMR signal from Pt(1) site is only one for whole temperature range [2], the magnetic structure of Fig. 3(b) should be deleted. Moreover, a kink at $T_{\rm N}$ in $\chi_{//c}$ of single crystal [3] supports that the magnetic moment is parallel to the *c*-axis. Anyway, our NMR spectrum is inconsistent with the magnetic structure obtained by the neutron diffraction experiment.

Now, an effective field ($H_{\rm eff}$) at constituent nuclei can be approximately expressed as $\mathbf{H}_{\rm eff} = \mathbf{H}_0 + \mathbf{H}_{\rm int}$. When powders of polycrystalline sample are randomly fixed, the direction of internal field is also randomly distributed in the AF state. A central peak corresponding to the perpendicular direction to an external field is affected by an internal field. The shift of a central peak is estimated as about $6\times10^{-4}$ T ($= |\mathbf{H}_0 + \mathbf{H}_{\rm int}| - H_0 = (H_0^2 + H_{\rm int}^2)^{1/2} - H_0, \because \mathbf{H}_0 \perp \mathbf{H}_{\rm int}$) 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.

In our recent specific heat experiments, the well "annealed" $Ce_{1.01}Pt_3Si$ sample shows a sharp and steep jump at 0.5 K for SC transition and also has a clear and large jump at 2.2 K associated with an AF transition, as displayed in Fig. 4. On the other hand, "as

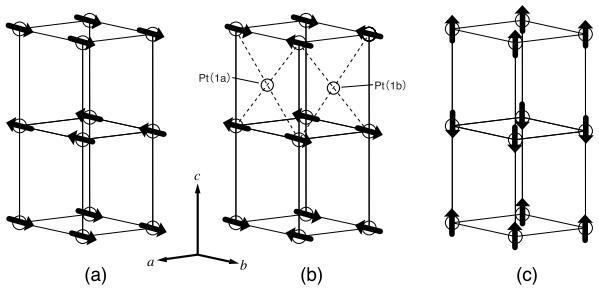


**FIGURE 3.** Magnetic structures of $CePt_3Si$. Arrows indicate the direction of the magnetic moment at Ce site. (a) A magnetic structure proposed by Metoki *et al.* (b) One of the magnetic structures to make the *c*-axis component with the moment lying in the basal *c*-plane. (see text) (c) A possible magnetic structure with the magnetic moment along the *c*-axis.

cast" $CePt_3Si$ sample shows a broad peak of SC transition at 0.75 K and a broad and low bump corresponding to the 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. Details will be published in elsewhere [7]. These results remind us high possibility of coexistence of two phases, which are composed of an AF phase and a paramagnetic like phase with a 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. 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. 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. This issue is quite reasonable for the spectrum of $^{29}Si$ NMR below $T_N$. Namely, the widely spread rectangular spectrum and a 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 full line width for a randomly fixed sample in the AF state is estimated as 0.048 T corresponding to $2H_{int}$. However, the observed width was 0.01 T at 1.3 K, as shown in Fig. 1(b). This may be due to presence of two phases or of complicated magnetic structures (*e.g.* SDW). This discrepancy of the line width cannot be understood at present.

In our previous nuclear relaxation time ($T_1$) measurements of $^{195}Pt$ and $^{29}Si$ [1], a long component of the $T_1$, which corresponds to a relaxation from the SC region, appeared below 0.5 K, although the reduced $T_c$ by a magnetic field exceeds 0.5 K. This result is probably due to a small inclusion of "high $T_c$ phase" even in our "annealed" samples. Spin-lattice relaxation rate ($1/T_1$) and Knight shift ($K$) were measured at a central peak, where an applied field is perpendicular to the *c*-axis. No remarkable enhancement in $1/T_1$ just below $T_c$ and no significant decrease in $K$ across $T_c$ were observed [1, 2]. If a coexistence of two phases (i.e. AF and paramagnetic like) is realized even in a single crystal with high quality, the temperature dependence of $K$ across $T_c$ for a central peak

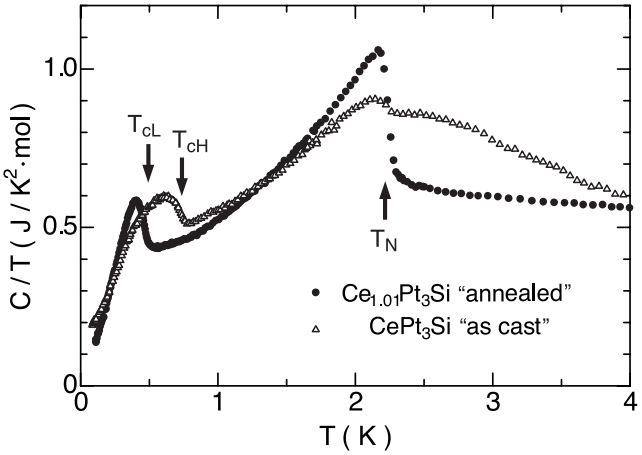


**FIGURE 4.** Temperature dependence of the specific heat in the form of $C/T$ of $CePt_3Si$. Closed circles and open triangles show the data of "annealed" sample and "as cast" sample, respectively. $T_{cL}$ and $T_{cH}$ mean low $T_c$ and high $T_c$, respectively. (see text)

and both ends of spread spectrum is required to discuss the spin state in the SC state precisely.

In conclusion, the NMR spectrum of $^{29}$Si cannot 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. Although the mechanism on difference of the line width in the spectrum is not clear, a scenario of coexistence composed of two phases can explain the $^{29}$Si spectrum very well. If the volume fraction of "high $T_c$ phase" in "as cast" $CePt_3Si$ sample is not negligible, "high $T_c$ phase" probably hides the behavior of an intrinsic relaxation rate in the SC state. For "annealed" and "as cast" samples, a central signal in "high $T_c$ phase" overlap with an $\mathbf{H}\perp c$ signal in "low $T_c$ phase".

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