\[ \text{\textsuperscript{121}Sb-NMR Knight shift study of filled skutterudite CeOs}\textsubscript{4}Sb\textsubscript{12} \]

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Abstract. We carried out a \textsuperscript{121}Sb nuclear magnetic resonance (NMR) measurement on CeOs\textsubscript{4}Sb\textsubscript{12} to investigate its electric state. The precise temperature \((T)\) dependence of the Knight shift was obtained by using an aligned powdered sample and NQR parameters. The \(T\) dependence of the Knight shift below 300 K cannot be explained by the \(c-f\) hybridization gap model with \(2D = 3000\) K and \(2\Delta = 320\) K obtained by the \(1/T_1\). This result indicates that there is \(q\)-dependence in the gap. It was revealed that a ferromagnetic correlation develops with decreasing temperature below 50 K from an increase of the Knight shift. Considering this result and previous \(1/T_1\) measurements, there are both ferromagnetic and antiferromagnetic fluctuations in CeOs\textsubscript{4}Sb\textsubscript{12}.

1. Introduction

Filled skutterudite compound ReTx\textsubscript{4}Pn\textsubscript{12} (Re = rare earth; Tx = Fe, Ru and Os; Pn = P, As and Sb) shows various ground states in many combinations of Re, Tx and Pn atoms. These varieties of intriguing phenomena arise from the characteristic crystal structure of the filled-skutterudite compounds (space group: \(Im\bar{3}, T_5^h\) No.204); twelve pnictogen atoms surround a rare-earth ion, which causes strong hybridization between conduction and \(f\)-electrons. Among filled-skutterudite compounds, most Ce-based compounds show insulating or semiconducting behavior, on the basis of which they are called hybridization-gap semiconductors. The magnitude of the gap is related to a lattice constant of the crystal, which collapses for Sb-based compounds [1]. However, CeOs\textsubscript{4}Sb\textsubscript{12}, which has the largest lattice constant among CeTx\textsubscript{4}Pn\textsubscript{12} compounds, exhibits Kondo insulating behavior in electric resistivity with a very small gap \(\Delta/k_B \sim 10\) K [2]. A large specific heat coefficient \(\gamma \sim 92\) mJ/K\textsuperscript{2}mol was also reported [3]. We previously reported that CeOs\textsubscript{4}Sb\textsubscript{12} has a hybridization gap of \(2\Delta/k_B \sim 320\) K, though a large residual density of states exists within the gap, as determined from a measurement of the nuclear spin-lattice relaxation rate \(1/T_1\) [4]. Furthermore, the nuclear spin-lattice relaxation rate \(1/T_1\) was observed to show an increase in spin fluctuation on the verge of an antiferromagnetic (AFM) quantum critical point (QCP) below 20 K. Moreover, CeOs\textsubscript{4}Sb\textsubscript{12} was reported to exhibit AFM order at...
(approximately \( T \sim 1 \) K and \( H = 0 \) [5]). A discriminative \( H - T \) phase diagram was obtained by resistivity, specific heat and \( ^{121}\text{Sb-NMR} \) measurements \([1, 3, 6]\).

In order to investigate the electric state of \( \text{CeOs}_4\text{Sb}_{12} \) further, we carried out an Sb-NMR experiment and measured the precise temperature (\( T \)) dependence of the Knight shift.

2. Experimental
A single crystal of \( \text{CeOs}_4\text{Sb}_{12} \) was prepared by the Sb-flux method [1]. For the NMR measurements, the sample was powdered to facilitate applied rf-field penetration. Pulse NMR measurements were performed on two Sb isotopes \( ^{121}\text{Sb} \) (\( I = 5/2 \), \( ^{121}\gamma/2\pi = 10.189\text{MHz/T} \) and \( ^{121}Q = -0.543 \times 10^{-28} \text{m}^2 \)) and \( ^{123}\text{Sb} \) (\( I = 7/2 \), \( ^{123}\gamma/2\pi = 5.5176\text{MHz/T} \) and \( ^{123}Q = -0.692 \times 10^{-28} \text{m}^2 \)) using the conventional spin-echo method in the range of \( T = 1.5 - 300 \) K. Here, \( I \), \( \gamma \) and \( Q \) are the nuclear spin, the nuclear gyromagnetic ratio and the nuclear quadrupole moment, respectively. The NMR spectrum was obtained by integrating a spin-echo signal point by point as a function of the magnetic field.

3. Results and Discussion
The electric field gradient at the Sb site is quite large and non-axially symmetric in the filled skutterudite compound; therefore, the nuclear quadrupole frequency increases. For example, \( \text{CeOs}_4\text{Sb}_{12} \) has the nuclear quadrupole frequency \( ^{121}\nu_Q \) \( (^{123}\nu_Q) = 43.847(26.628) \text{MHz} \) with asymmetry parameter \( \eta = 0.463 \) at \( T = 4.2 \) K [4]. Therefore, a broad complex NMR spectrum would be expected for a powdered sample. However, as shown in Fig. 1(a), we observed many sharp peaks close to the case of the spectrum using a single crystal. This is because \( \text{CeOs}_4\text{Sb}_{12} \) has a small anisotropy of magnetization above \( \sim 2 \) T \( (M^{[100]} > M^{[110]} > M^{[111]}) \), and the powdered sample is aligned to \( H \parallel [100] \). Although Sb has two isotopes, namely, \( ^{121}\text{Sb} \) and \( ^{123}\text{Sb} \), most of the peaks arise from \( ^{121}\text{Sb} \) because of the differences in nuclear gyromagnetic ratio \( \gamma_n \) and nuclear quadrupole frequency \( \nu_Q \). The filled skutterudite structure...
has one crystallographically equivalent Sb site; however, three $^{121}$Sb NMR spectra appear for $H \parallel [100]$ owing to the anisotropy of the Sb 24g site \cite{7}. Among them, we focused on Sb(1) site, which is located in $H \parallel [100] \parallel V_{zz}$, for a measurement of the Knight shift in this study. Here, $V_{zz}$ is the main principal axis of the electric field gradient (EFG) at the Sb position.

The nuclear spin Hamiltonian in the case of $H \parallel V_{zz}$ is given by

$$
\mathcal{H} = -\gamma_n h (1 + K) H_0 I_z + \frac{h \nu_Q}{6} \left[ 3I_z^2 - I^2 + \eta (I_x^2 - I_y^2) \right].
$$

(1)

The first term of the Hamiltonian represents the Zeeman interaction between the $^{121}$Sb nuclear spin $I$ and the applied field $H_0$. $K$ is the Knight shift caused by a hyperfine interaction between the nucleus and electrons, and is related to the spin susceptibility. The second term in the Hamiltonian represents the nuclear quadrupole interaction between the EFG and the $^{121}$Sb nuclear quadrupole moment. Here, $\nu_Q$ is defined by $\nu_Q \equiv 3eQV_{zz}/2I(2I - 1)h$, and $\eta$ is the asymmetry parameter defined by $\eta = (V_{xx} - V_{yy})/V_{zz}$, which is a measure of the deviation from the axial symmetry of the EFG tensor. The numerically calculated field-swept NMR spectrum for the Sb(1) site is shown in Fig. 1(b) which well explains some of peaks of the experimental result. Here, we assumed $K = 0$. Other peaks are attributed to the Sb(2) and Sb(3) sites, respectively.\cite{6} Figure 1(c) shows the numerical calculation of the resonance frequency at the $^{121}$Sb(1) site as a function of $\mu_0H$. As for the measurement of the Knight shift, we used a transition at $f = 148.1$ MHz and $H \sim 6$ T.

We measured the NMR spectrum around 6 T and determined the resonance field at each $T$. The closed circles in Fig. 2 represent the $T$ dependence of the resonance field, which indicates strong $T$ dependence. However, this does not directly indicate $T$ dependence of the Knight shift. This is because $^{121}\nu_Q$ and $\eta$ also show $T$ dependence. To estimate the precise $T$ dependence of the Knight shift, we measured the $T$ dependence of $^{121}\nu_Q$ and $\eta$, then we calculated the resonance fields in the case of $K = 0$. From these data, we obtained the Knight shift using the relation $K = (H_0 - H_m)/H_m$. Here, $H_0$ is the resonance field in the case of $K = 0$ (open circles in Fig. 2), and $H_m$ is the experimental result (closed circles in Fig. 2).
Figure 3(a) shows the $T$ dependence of the Knight shift, which shows a slight increase as $T$ decreases below 300 K. We try to explain this behavior using the $c-f$ hybridization gap model with a rectangular shape of the density of states (DOS) as shown in the inset of Fig. 3. As for $1/T_1$, this model explains well the $T$ dependence with parameters $2D = 3000$ K and $2\Delta = 320$ K [4]. However, these parameters can not explain the variation of the Knight shift. If we choose smaller values of $2D$ and $2\Delta$, this model can explain the $T$ variation of the Knight shift above 50 K. For example, the solid line in Fig. 3 is a calculation with $2D = 1400$ K and $2\Delta = 0$ K, which fits the data well. This discrepancy of the gap size might be caused by the $q$-dependence of the gap. The Knight shift shows an apparent increase as $T$ decreases below $\sim 50$ K, indicating the development of a ferromagnetic correlation because the Knight shift probes spin susceptibility $\chi_s = (0, 0)$. From this result and our previous $T_1$ experiment, it is indicated that there are both ferromagnetic and antiferromagnetic fluctuations in CeOs$_4$Sb$_{12}$. The anomalous ordered phase above $\sim 1$ T is considered to be caused by such complex electron correlations.

4. Summary
In summary, we have performed Sb-NMR measurement on CeOs$_4$Sb$_{12}$. The powdered sample is aligned to $H \parallel [100]$, which allows us to estimate a precise value of the Knight shift even where the $\nu_Q$ and $\eta$ are large. The $T$ dependence of the Knight shift below 300 K can not be explained by the $c-f$ hybridization gap model with $2D = 3000$ K and $2\Delta = 320$ K obtained by the $1/T_1$. This result indicates that there is $q$-dependence in the gap. It was revealed from an increase of the Knight shift that a ferromagnetic correlation develops as $T$ decreases below 50 K. Considering this result and previous $1/T_1$ measurements, it can be concluded that there are both ferromagnetic and antiferromagnetic fluctuations in CeOs$_4$Sb$_{12}$.

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References
[1] Sugawara H, Osaki S, Kobayashi M, Namiki T, Saha S R, Aoki Y and Sato H 2005 Phys. Rev. B 71 125127.
[2] Bauer E D, Slebarski A, Freeman E J, Sirvent C and Maple M B 2001 J. Phys.: Condens. Matter 13 4495.
[3] Namiki T, Aoki Y, Sugawara H, and Sato H 2003 Acta Phys. Pol. B 34 1161.
[4] Yogi M, Kotegawa H, Zheng G-q, Kitaoka Y, Ohsaki S, Sugawara H and Sato H 2005 J. Phys. Soc. Jpn. 74 1950.
[5] Iwasa K, Itobe S, Yang C, Murakami Y, Kohgi M, Kuwahara K, Sugawara H, Sato H, Aso N, Tayama T, and Sakakibara T 2007 J. Phys. Soc. Jpn. 77 Suppl. A 318.
[6] Yogi M, Niki H, Yashima M, Mukuda H, Kitaoka Y, Sugawara H, and Sato H 2009 J. Phys. Soc. Jpn. 79 053703.
[7] Tou H, Doi M, Sera M, Yogi M, Kitaoka Y, Kotegawa H, Zheng G-q, Harima H, Sugawara H, Sato H 2005 Physica B 395-361 892.