Charge Fluctuation in Ce-based Filled-Skutterudite

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Abstract. We carried out $^{121,123}$Sb nuclear quadrupole resonance (NQR) measurement on CeOs$_4$Sb$_{12}$ to investigate an anomaly observed in ReOs$_4$Sb$_{12}$. The full width of half maximum of the NQR spectrum shows a step-like increase at 115 K with decreasing temperature ($T$). The nuclear spin-spin relaxation rate $1/T_2$ also shows a divergence at the same $T$. These results are considered to be caused by a distribution of the electric field gradient (EFG) and its fluctuation, which might arise from a small deformation of the cage which consists of twelve Sb. It is considered that the anomaly observed in ReOs$_4$Sb$_{12}$ at $T \sim 120$ K is originated from an unique crystal structure of the filled skutterudite.

1. Introduction

Filled skutterudite compound ReT$_4$X$_{12}$ (Re = rare earth; T = Fe, Ru and Os; X = P, As and Sb) exhibits various ground states by many combination of Re, T and X atoms. Among them, ReOs$_4$Sb$_{12}$ compounds have attracted much attention because of their characteristic properties, for example, heavy fermion superconductivity for PrOs$_4$Sb$_{12}$ [1] and unique heavy fermion state for SmOs$_4$Sb$_{12}$ [2]. Meanwhile, most of Ce-based skutterudite compounds show insulating or semiconducting behavior which is due to a hybridization between $f$- and conduction electron, so-called hybridization gap. CeOs$_4$Sb$_{12}$ is also reported to be a semiconductor with a small gap of $\Delta/k_B \sim 10$ K [3]. Our previous measurement of Sb nuclear quadrupole resonance (NQR) reveals an existence of $c-f$ hybridized gap with a finite residual density of state inside the gap.[4] Furthermore, a development of the low-energy spin fluctuation with decreasing temperature ($T$) below 25 K is observed by an enhancement of $1/T_1T$.

On the other hand, Kotegawa et al. reported an anomaly at $\sim 120$ K for ReOs$_4$Sb$_{12}$ (Re = La, Pr, Sm) from measurements of Sb-NQR spectrum and the nuclear spin-spin relaxation time $T_2$ [5]. A divergence of $1/T_2$ at $\sim 120$ K observed in ReOs$_4$Sb$_{12}$ (Re = La, Pr, Sm) is considered to be caused by some kind of lattice anomaly, and they speculated that a small distortion in the Sb cage occurs at $\sim 120$ K.

In order to investigate this anomaly further, we carried out Sb-NQR measurement on CeOs$_4$Sb$_{12}$. As mentioned above, CeOs$_4$Sb$_{12}$ shows semiconducting behavior, as contrasted with metallic behavior of ReOs$_4$Sb$_{12}$ (Re = La, Pr, Sm). If the anomaly is an inherent characteristic
in the skutterudite structure, it is speculated that a divergence of $1/T_2$ is also observed in CeOs$_4$Sb$_{12}$. In this paper, we report on the Sb-NQR spectra and $1/T_2$.

2. Experimental

Single crystal of CeOs$_4$Sb$_{12}$ was prepared by the Sb-flux method [6]. For the NQR measurement, the sample was powdered to facilitate applied rf-field penetration. The pulse NQR measurement was performed on two Sb isotopes $^{121}$Sb ($I = 5/2$, $^{121}\gamma/2\pi = 10.255$ MHz/T and $^{121}Q = -0.36 \times 10^{-28}$ m$^2$) and $^{123}$Sb ($I = 7/2$, $^{123}\gamma/2\pi = 5.5532$ MHz/T and $^{123}Q = -0.49 \times 10^{-28}$ m$^2$) using the conventional spin-echo method at zero field and in the range of $T = 80 - 300$ K. Here, $I$, $\gamma$ and $Q$ are the nuclear spin, the nuclear gyromagnetic ratio and the nuclear quadrupole moment, respectively. The NQR spectrum was obtained by integrating a spin-echo signal point by point as a function of frequency. The nuclear spin-spin relaxation time $T_2$ was obtained by integrating the spin-echo signal $M(2\tau)$ as a function of time $2\tau$, where $\tau$ is the time separation between $\pi/2$ and $\pi$ pulses.

3. Results and Discussion

Five Sb-NQR spectra were observed for CeOs$_4$Sb$_{12}$ with nuclear quadrupole frequency $^{121}\nu_Q(^{123}\nu_Q) = 43.84\text{MHz}(26.628)$ MHz and asymmetry parameter $\eta = 0.463$ from our previous work [4]. Among them, we used $2\nu_Q$, or $|\pm 3/2\rangle \leftrightarrow |\pm 5/2\rangle$ transition, for both $^{121}$Sb and $^{123}$Sb nuclei in this study. Figure 1 shows $^{123}$Sb-2$\nu_Q$ spectrum at 80 and 140 K. The full width at half maximum (FWHM) of the spectrum at 140 K is about 50 kHz, indicating a high quality of the sample composition. Ordinarily, if there is no phase transition, e.g. magnetic ordering, a FWHM shows almost $T$ independent or continuous $T$ dependence. Therefore, a slight increase of FWHM at 80 K compared with 140 K seems usual behavior. However, as shown in Fig. 2, the FWHM exhibits step-like increase at $\sim 115$ K, indicating clear anomaly. Because of no magnetic anomaly in this $T$ region, it is considered that a distribution of the electric field gradient (EFG) tensor, $V_{\alpha\beta} = \partial^2 V/\partial x_\alpha \partial x_\beta$ ($\alpha, \beta = x, y, z$), where $V$ is the electrostatic potential at the nuclear position, is an origin of the broadening of the spectrum. On the other hand, the peak position of the NQR spectrum, which is proportional to $V_{zz}$, does not show clear anomaly at $\sim 115$ K although the peak frequency starts to decrease below 140 K (figure not shown).

To investigate this property more accurately, we measured $1/T_2$ for both Sb isotopes. Figure

![Figure 1. $^{123}$Sb NQR spectrum for $2\nu_Q$ transition at 80 K (open triangle) and 140 K (closed circle).](image)

![Figure 2. $T$ dependence of the FWHM at $^{123}$Sb-2$\nu_Q$. The solid line is a guide for the eye.](image)
Figure 3. $^{123}\text{Sb}$ nuclear magnetization decay curve $M(2\tau)$. The $M(2\tau)$ is well fitted by an exponential function $M(2\tau) \propto \exp(-2\tau/T_2)$ as shown by the solid line.

3 displays the spin echo decay curve $M(2\tau)$ as a function of $2\tau$ for $^{123}\text{Sb}-2\nu Q$ at 300 K. It is apparent that $M(2\tau)$ shows exponential decay and follows the relation $M(2\tau) \propto \exp(-2\tau/T_2)$ as shown in the solid line in Fig. 2. The decay curve for $^{121}\text{Sb}$ also shows similar behavior as that for $^{123}\text{Sb}$.

$T$ dependences of $1/T_2$ for both Sb isotopes are displayed in Fig. 4(a). It is apparent that $1/T_2$’s exhibit a peak at $T = 115$ K, where the NQR spectrum showed broadening. Contrary to this, the nuclear spin-lattice relaxation rate $1/T_1$’s show no sign of the anomaly around $T = 115$ K as shown in Fig. 4(b). In general, $1/T_1(1/T_2)$ is affected by fluctuations perpendicular(parallel + perpendicular) to the principal axis of the EFG around nucleus, hence this contrasting behavior of $1/T_1$ and $1/T_2$ seems to indicate an anisotropy of the fluctuations. For $1/T_1$, it is revealed that a magnetic fluctuation is a predominant relaxation process from the relation $^{123}T_1^{-1}/^{121}T_1^{-1} \simeq (^{123}\gamma/^{121}\gamma)^2 = 0.293$. This relation is also expected for $1/T_2$ where a magnetic relaxation is dominant [7]. However, it is not applicable to $^{123}T_2^{-1}/^{121}T_2^{-1} = 0.76 \pm 0.03$. As for $1/T_1$, if a quadrupole relaxation process is a predominant relaxation process, it is expected that a ratio of the relaxation rate becomes $^{123}Q^2 f(7/2)/^{121}Q^2 f(5/2) = 0.78$ where spin dependence factors are given by $f(I) = (2I + 3)/I^2(2I + 1)$ [8]. Hence, if this relation can apply to the ratio of $1/T_2$, it is inferred that the quadrupole relaxation process, which might be caused by the fluctuation of the EFG tensor, is important for $1/T_2$.

Since the $T$ where the $1/T_2$ showed a peak and the NQR spectrum showed a broadening is almost the same as other ReOs$_4$Sb$_{12}$ compounds, we consider that the skutterudite structure is related to the anomaly and the EFG fluctuation is caused by a charge fluctuation which comes from a small deformation of the cage consist of twelve Sb surrounding rare earth ion.

4. Summary
In summary, we have performed Sb-NQR measurement on CeOs$_4$Sb$_{12}$. The FWHM of the NQR spectrum indicates step-like increase below $T = 115$ K, and $1/T_2$ shows a significant peak at the same $T$. A quadrupolar relaxation process derived from a fluctuation of the EFG tensor is predominant for $1/T_2$, although $1/T_1$ process is predominated by the magnetic fluctuation. From these results, the observed anomaly at $T \sim 120$ K for ReOs$_4$Sb$_{12}$ (Re = La, Pr, Sm and Ce) compounds is considered to be caused by a small Sb-cage deformation. To clarify an effect of $d$-electron in this anomaly, it is needed to do the same measurement for other filled skutterudite, e.g. CeRu$_4$Sb$_{12}$, and now in progress.

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Figure 4. (a) $T$ dependences of $1/T_2$ for both $^{121}$Sb (closed circle) and $^{123}$Sb (open circle). (b) $T$ dependences of $1/T_1$ for both $^{121}$Sb (closed square) and $^{123}$Sb (open square).

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Acknowledgments

References

[1] Bauer E D, Frederick N A, Ho P -C, Zapf V S, Maple M B 2002 Phys. Rev. B 65 100506(R)
[2] Sanada S, Aoki Y, Aoki H, Tsuchiya A, Kikuchi D, Sugawara H and Sato H 2005 J. Phys. Soc. Jpn. 74 246
[3] Bauer E D, `Slebarski A, Freeman E J, Sirvent C and Maple M B 2001 J. Phys.: Condens. Matter 13 4495
[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] Kotegawa H, Hidaka H, Kobayashi T C, Kikuchi D, Sugawara H and Sato H 2007 Phys. Rev. Lett. 99 156408
[6] Sugawara H, Osaki S, Kobayashi M, Namiki T, Saha S R, Aoki Y and Sato H 2005 Phys. Rev. B 71 125127
[7] Pennington C H, Durand D J, Slichter C P, Rice J P, Bukowski E D, Ginsberg D M 1989 Phys. Rev. B 39 274
[8] Mieher R L 1962 Phys. Rev. 125 1537