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Connection between Charge Fluctuations and the Coherent Temperature in the Heavy-Fermion System SmOs$_4$Sb$_{12}$: A $^{121,\,123}$Sb NQR Study

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We report $^{121,\,123}$Sb nuclear quadrupole resonance measurements under pressure in a novel heavy fermion (HF) system SmOs$_4$Sb$_{12}$. The nuclear spin-spin relaxation rate $1/T_2$ exhibits a distinct peak near the coherent temperature of the Kondo effect. The isotope effect of ^{121}Sb and ^{123}Sb indicates that the peak in $1/T_2$ is electrical in origin. The connection between the peak in $1/T_2$ and the development of coherency of the Kondo effect is robust even under pressure. It is conjectured that charge fluctuation plays an important role in forming the HF state in SmOs$_4$Sb$_{12}$.

Recent material development of skutterudite compounds has lead to the discovery of some new heavy fermion (HF) systems in Pr- and Sm-based compounds [1–5]. One characteristic of skutterudite compounds is that the rare-earth-metal ion is located in a highly symmetric position within a cage structure composed of 12 pnictogen atoms. This yields a large number of degeneracy (N) for the crystal electric field (CEF) levels and strong hybridization between the f-electrons and the conduction electrons (c-f hybridization), which increases the Kondo temperature. On the other hand, the large N gives rise to multipole moments, which can influence low-temperature properties in some compounds [6–8]. The anharmonic vibration of the rare-earth-metal ion in the cage, the so-called "rattling" motion, has been reported in compounds having a filled-cage structure, including skutterudite compounds [9–12] and other compounds [13,14]. It has been pointed out that quantum tunneling between the potential minima dominates over thermal rattling at low temperatures in PrOs$_4$Sb$_{12}$ [10]. The HF state induced by such ionic motion has been proposed theoretically [15,16]. Thus, an HF state of nonmagnetic origin is capable of being induced in skutterudite compounds.

SmOs$_4$Sb$_{12}$ is a unique HF system with a large electronic specific heat coefficient of $\gamma_e \sim 800$ mJ/mol K^2 [4,5]. A mixed-valence state of Sm^{3+} and Sm^{2+} has been reported [17,18]. The most remarkable feature is the robustness of mass enhancement against magnetic field, in contrast to Ce-based HF systems. Although Lande's g-factor g_J of the Sm^{3+} ion is 1/3 that of the Ce^{3+} ion, it is considered that by itself this small value of g_J is unable to explain the insensitivity of γ_e to magnetic fields, and it is conjectured that there is some electric contribution to the formation of the HF state in SmOs$_4$Sb$_{12}$.

In this Letter, we report new results for $^{121,\,123}$Sb-NQR measurements under pressure, comparing them with the previous resistivity data [19]. The samples were prepared by the same manner as Ref. [4,19]. NQR measurements

under pressure were carried out utilizing a piston-cylinder cell. Daphne oil 7373 is used as a pressure-transmitting medium. The applied pressure was estimated from the superconducting transition temperature of lead.

Figure 1 shows the temperature dependence of the $4f$-electron contribution $(1/T_1)_{4f}$ at several pressures, obtained by subtracting $1/T_1$ for LaOs$_4$Sb$_{12}$ from the raw data [20]. The $(1/T_1)_{4f}$ exhibits a kink near $T^* \sim 20$–25 K, as reported previously [19]. The resistivity also decreases rapidly below T^*. The inset shows $1/T_1$ measured for both ^{121}Sb and ^{123}Sb. ^{121}Sb (^{123}Sb) has a natural abundance of 57.3% (42.7%), a nuclear spin of $I = 5/2$ (7/2), a nu-
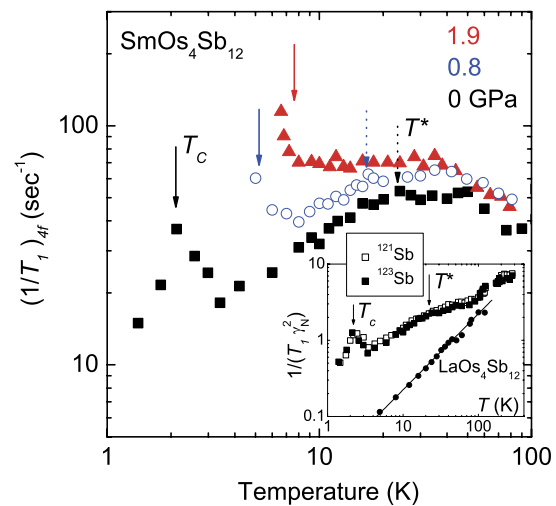

FIG. 1 (color online). Temperature dependence of $(1/T_1)_{4f}$ for $2\nu_Q$ transition of ^{123}Sb. The inset shows the comparison of $1/(T_1\gamma_N^2)$ measured for ^{121}Sb and ^{123}Sb. The NQR intensity weakens around T_C, disappearing at low temperatures. At ambient pressure, the intensity decreases to $\sim$20% of the expected value at 1.4 K. Under pressure, on the other hand, the signal disappears without showing the peak in $1/T_1$. The cause is not clarified at the present stage. The arrows at 0.8 and 1.9 GPa indicate T_C determined by the resistivity measurements.

clear gyromagnetic ratio of $\gamma_N = 10.189\,(5.5175)$ MHz/T, and a nuclear quadrupole moment of $Q = -0.59(-0.75) \times 10^{-24}$ cm^2 [21]. We can check whether the relaxation mechanism is magnetic or electric from the differences in γ_N and Q between ^{121}Sb and ^{123}Sb. The good agreement for $1/(T_1\gamma_N^2)$ of ^{121}Sb and ^{123}Sb suggests that the $1/T_1$ is dominated by magnetic relaxation. This fact strongly suggests that the reduction in $(1/T_1)_{4f}$ below T^* is magnetic in origin, that is, the conduction electrons screen the magnetic moment due to the Kondo effect. The T^* determined by $(1/T_1)_{4f}$ decreases with increasing pressure, which is the same tendency as that observed for the resistivity [19]. The $(1/T_1)_{4f} = $ constant behavior above T^* arises from the Ruderman-Kittel-Kasuya-Yosida interaction between localized moments. The fact that the value of the constant increases when pressure is applied suggests an increase in the effective moment and/or a decrease in J_{cf} (the exchange interaction between conduction electrons and f-electrons) [22]. The kink on the high-temperature side (~ 50 K at ambient pressure), which is approximately J_{cf}, also decreases under pressure. These effects of pressure on $(1/T_1)_{4f}$ are the opposite of those observed in Ce-based HF systems [22]. All these behaviors in $1/T_1$ demonstrate the "magnetic" Kondo effect and its coherent state below T^*.
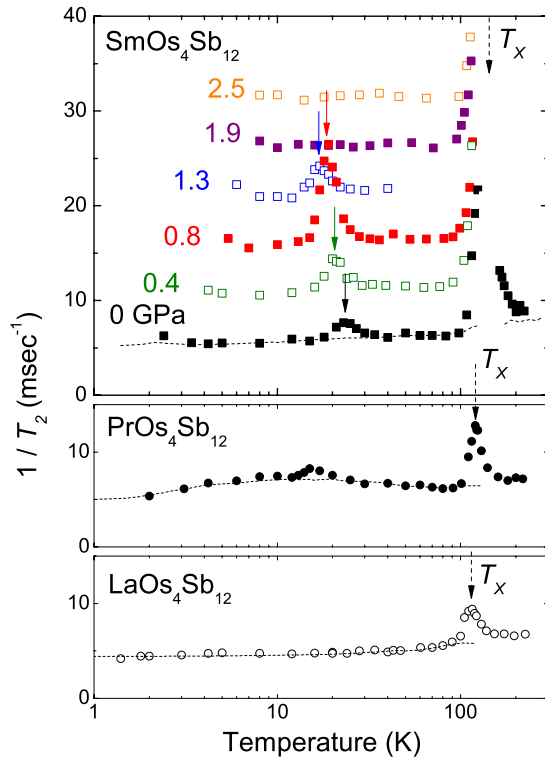
Figure 2 shows the temperature dependencies of $1/T_2$ for various pressures. For comparison, we measured $1/T_2$ for PrOs$_4$Sb$_{12}$ (HF superconductor) [2] and LaOs$_4$Sb$_{12}$. T_2 was determined by fitting a single exponential function to the spin-echo decay curve. Distinct peaks are observed at T_X in all systems, as indicated by the dotted arrows in the figure. T_X is slightly dependent on the rare-earth-metal ion ($T_X \sim 115$ K for LaOs$_4$Sb$_{12}$, 120 K for PrOs$_4$Sb$_{12}$, and 125–150 K for SmOs$_4$Sb$_{12}$). A similar temperature dependence of $1/T_2$ has been obtained for LaOs$_4$Sb$_{12}$ by another group [12]. The NQR signal in SmOs$_4$Sb$_{12}$ disappears between 125–150 K due to the short T_2. On the other hand, other peaks are observed near 20 K in SmOs$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$.

The dotted curves in Fig. 2 were calculated using $a + b \times (1/T_1)$ with $a = 5$ msec^{-1} and $b = 15$ for SmOs$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$, and $a = 4.4$ msec^{-1} and $b = 20$ for LaOs$_4$Sb$_{12}$. The constant value a is considered to originate from the nuclear dipole interaction, and the latter term is the contribution of the electron spins. With the exception of the peaks, these curves reproduce $1/T_2$ well, indicating that the peaks originate from another contribution. Figure 3(b) shows $1/T_2$ of ^{121}Sb and ^{123}Sb for SmOs$_4$Sb$_{12}$. A quantitative comparison of $1/T_2$ for ^{121}Sb and ^{123}Sb is difficult since T_2 generally depends on the ratio of the rf pulse $\gamma_N H_1$ and the NQR spectral width, which differs for the measured $1\nu_Q$ transition for ^{121}Sb and the $2\nu_Q$ transition for ^{123}Sb. For a relative comparison, the $1/T_2$ for ^{121}Sb are normalized to those for ^{123}Sb in the

FIG. 2 (color online). Temperature dependences of $1/T_2$ for $2\nu_Q$ transition of ^{123}Sb in SmOs$_4$Sb$_{12}$ for various pressures, PrOs$_4$Sb$_{12}$, and LaOs$_4$Sb$_{12}$. The data for SmOs$_4$Sb$_{12}$ under various pressures are shifted upward for clarity. T_2 was measured by fixing the width of $\pi/2$ pulse and π pulse. The dotted curves indicate the magnetic contribution (see text).
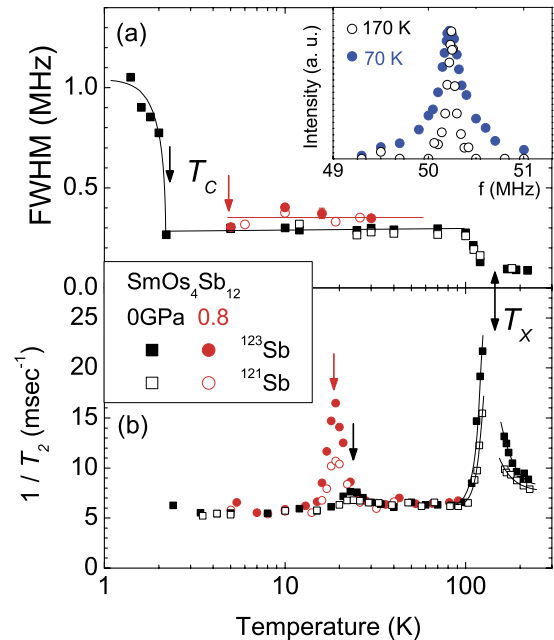

FIG. 3 (color online). Temperature dependence of (a) FWHM and (b) $1/T_2$ measured for ^{121}Sb and ^{123}Sb in SmOs$_4$Sb$_{12}$. The data for ^{121}Sb are normalized to the data for ^{123}Sb. The respective factors are 0.8 for FWHM and 0.46 for $1/T_2$, irrespective of pressure. The inset shows the spectra for $2\nu_Q$ transition of ^{123}Sb at 170 and 70 K. All the lines are guides for the eye.

measured temperature range, ignoring the peaks. The observed peaks are larger in ^{123}Sb than in ^{121}Sb, suggesting that the origin of the peaks is electric. Similar isotope effects are also observed for all the peaks of $PrOs_4Sb_{12}$ and $LaOs_4Sb_{12}$. The linewidth of the Sb-NQR spectrum (FWHM) increases just below T_X as shown in Fig. 3(a) and the inset. This also supports the proposition that the anomaly in $1/T_2$ is electric in origin. The $1/T_2$ is known to be the low-frequency component of the fluctuation along the quantum axis of the nuclear spin, which corresponds to the fluctuation of the nuclear spin splitting. Since the splitting is induced by the electric field gradient (EFG) at the Sb site, $1/T_2$ is sensitive to charge fluctuations through the fluctuation of the EFG at Sb sites. Similar behavior has been observed in $PrBa_2Cu_4O_8$, where slow charge fluctuations of electronic or ionic origin freeze at low temperatures [23]. In this system, analysis of T_1 shows that $1/T_2$ has a peak when the charge fluctuation crosses the correlation time of $\sim 10^{-6}$ sec.

Concerning the origin of the slowing down (or freezing) of the charge fluctuation at T_X, the presence of the anomaly in $LaOs_4Sb_{12}$ rules out the direct participation of f electrons, suggesting a lattice anomaly. The increase in FWHM

suggests that the 12 Sb sites are not equivalent below T_X. The exact origin is unclear, but we speculate that a small distortion in the Sb cage occurs below T_X.

On the other hand, other peaks are observed at ~ 20 K in $SmOs_4Sb_{12}$ (as indicated by the solid arrows in Figs. 2 and 3) and at ~ 15 K in $PrOs_4Sb_{12}$. In $SmOs_4Sb_{12}$, the temperature of the peak decreases with pressure, and the peak is enhanced, especially at 0.8 GPa. We cannot find a distinct change in the FWHM around 20 K even at 0.8 GPa within the experimental error as shown in Fig. 3(a). The strong broadening below T_X might mask small changes in the spectrum. Figure 4(a) shows the pressure-temperature phase diagram and the pressure-dependence of T^* determined by the resistivity and $1/T_1$. The two T^* exhibit good agreement with each other. The temperature of the peak at $1/T_2$ is also plotted in Fig. 4(a). The peak in $1/T_2$ is found to appear at T^*. The anomaly in $1/T_2$ disappears above 1.9 GPa, where $1/T_1$ does not show the coherent behavior as shown in Fig. 1. This suggests that the observed charge fluctuation is related to the development of coherency at T^*.

Figures 4(c)–4(e) show the pressure dependence of n, ρ_0, and A determined by resistivity (ρ) measurements [19]. The exponent n and the residual resistivity ρ_0 are estimated using $\rho(T) = \rho_0 + A'T^n$. n is approximately 2 at ambient pressure, which is Fermi liquid (FL) behavior. By contrast, n is less than 2 at 0.72 GPa, as shown in Fig. 5. This non-Fermi liquid-like (NFL) behavior is remarkable around 0.72 GPa, and the FL behavior recovers above ~ 2 GPa. The $1/T_2$ exhibits anomaly in the pressure range of the NFL-like behavior as shown in Figs. 4(b) and 4(c), where n has a minimum when the peak in $1/T_2$ is maximized. ρ_0 also has a broad peak in approximately the same pressure range. The coefficient A was deduced by fitting the data below ~ 0.5 K with $\rho = \rho_0 + AT^2$ coercively even in the range $n < 2$ [24], having a broad peak around 1 GPa. The
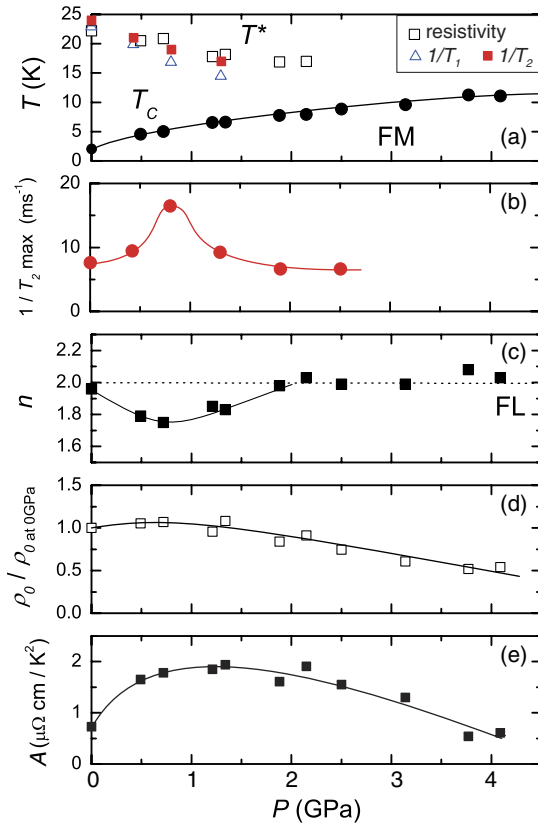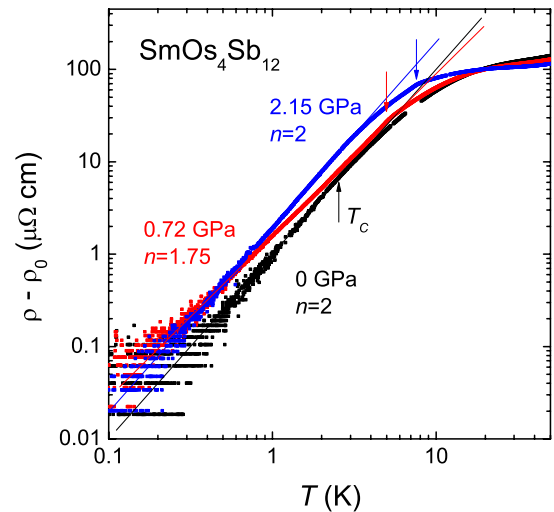
FIG. 4 (color online). (a) Pressure-temperature phase diagram of $SmOs_4Sb_{12}$. Temperatures showing the peak in $1/T_2$ (closed squares) are consistent with T^* determined by the resistivity (open squares) and $1/T_1$ (triangles). (b–e) Pressure dependence of the maximum value in $1/T_2$ around T^*, the exponent n, the residual resistivity ρ_0, and the coefficient A.

FIG. 5 (color online). ρ-ρ_0 vs temperature. ρ obeys the FL form of $n = 2$ at ambient pressure and 2.15 GPa, but $n = 1.75$ is observed at 0.72 GPa.

pressure-temperature phase diagram suggests that $SmOs_4Sb_{12}$ is located in the vicinity of the FM critical point [19]. It is difficult, however, to explain adequately the NFL-like behavior and the increase in A under pressure in the framework of the ''magnetic'' Kondo lattice system only. If we assume that the NFL-like behavior is related to the FM critical fluctuation, it should be remarkable at ambient pressure. It rather seems to relate to the anomaly in $1/T_2$. In Ref. [19], we tried to explain the increase in A under pressure by the pressure dependence of T^* through $A \propto (1/T^*)^2$, but it ignored the change in entropy at T_C although T_C increases under pressure. In most HF compounds exhibiting a magnetic critical point, A exhibits a maximum in the vicinity of the critical point. The increase in A around 1 GPa suggests the possibility of the direct mass enhancement by electric degree of freedom, although further investigation is required to establish it.

The peak in $1/T_2$ at low temperatures is absent in $LaOs_4Sb_{12}$, suggesting that f-electrons contribute to the peak at T^* in $SmOs_4Sb_{12}$. There are two possibilities for the origin of this charge fluctuation appearing in $1/T_2$. The first one is a fluctuation of the multipole moment as the direct f contribution. It is important to account for the level scheme of the CEF in $SmOs_4Sb_{12}$, but it has not yet been clarified. If the HF state of $\gamma_e \sim 800$ mJ/mol K^2 is attributable to only the $J = 5/2$ multiplet of Sm^{3+}, the large γ_e can be explained by the large number of degeneracy in the CEF levels ($N = 4$ or 6) [4,25]. These CEF states have a quadrupole moment and much higher multipole moments. If the anomaly of $1/T_2$ around T^* indeed originates from the fluctuation of the multipole moment, the Kondo effect of multipole moments (e.g., the quadrupolar Kondo effect [26]) might occur.

Another possible explanation of the peak in $1/T_2$ at T^* is the indirect contribution of the f-electrons. The anomaly in elastic constant suggesting the rattling motion has been reported in $PrOs_4Sb_{12}$ [10]. A similar anomaly has been observed in $SmOs_4Sb_{12}$ in the temperature range 10–20 K, which is close to T^* [27]. However, the peak in $1/T_2$ is absent in $LaOs_4Sb_{12}$, which is reported to have a similar rattling motion [11,12,28]. This discrepancy is explained by coupling between the f electrons and the EFG at the Sb site. The slow fluctuation of the rare-earth-metal ion with f-electrons is considered to induce fluctuations in the CEF state, the strength of the c-f hybridization, and the valence of the rare-earth-metal ion, which result in the fluctuation of the EFG at the Sb site. The slowing down of the rattling motion itself is one possible explanation of the peak in $1/T_2$, but if the rattling mode changes to another mode below T^* and each mode makes the different EFG at the Sb site, the change in the mode also may induce the fluctuation of the EFG, that is, the peak in $1/T_2$. The NFL-like behavior around 0.8 GPa seems to suggest the existence of some quantum fluctuation. This might indicate that Sm ion continues to move within the cage, contributing the mass enhancement as pointed out theoretically [15].

In summary, the temperature and pressure dependencies of $1/T_1$ demonstrate the occurrence of the magnetic Kondo effect and its coherent state below T^* in $SmOs_4Sb_{12}$, but the peak in $1/T_2$ at T^* indicates that the slowing down of the charge fluctuation is involved with the formation of the HF state. The T^* is considered to be determined by the coupling between the c-f hybridization and the charge fluctuation. This is one possible explanation for the robustness of mass enhancement against magnetic field. The HF state in $SmOs_4Sb_{12}$ is conjectured to be a new class induced by the interaction between the magnetic Kondo effect and the charge fluctuation. The charge fluctuation might originate from multipolar fluctuation or motion of Sm ion. Further investigation is required to elucidate this.

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