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NMR study of black-phase in SmS

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Abstract. We report the result of the ^{33}S nuclear magnetic resonance (NMR) measurement on the nonmagnetic semiconductor SmS at ambient pressure. For this measurement, the ^{33}S isotope enriched powder sample of SmS was prepared to increase the ^{33}S NMR intensity. We have attempted ^{33}S NMR measurement on SmS and successfully observed the signal of it. With decreasing temperature, the spectrum measured at the constant magnetic field shifted to lower frequency and became weakly temperature dependent below 50 K. The presence of the energy gap was microscopically established by the rapid decrease in the nuclear spin-lattice relaxation rate $1/T_1$. The activation energy was deduced to be 625 K from an Arrhenius plot of T_1.

1. Introduction

The valence transition of lanthanide compounds has attracted much attention because their physical properties drastically change due to the intimate relation between the valence and magnetic properties of $4f$ electrons. SmS shows the pressure-induced valence transition in which there is no change in symmetry[1]. At ambient pressure SmS is a nonmagnetic semiconductor where the samarium ions are divalent. According to Hund's Rule and a spin-orbit interaction, Sm^{2+} ion ($4f^6$) is in nonmagnetic ground state. An energy gap size was estimated to be ∼1000 K by the electrical resistivity[2, 3]. SmS undergoes the pressure-induced first-order transition from a semiconducting to a metallic phase under the pressure of 0.65 GPa. This transition alters the valence state of Sm from Sm^{3+} to the mixed valence of Sm^{2+} and Sm^{3+}, and the color of the sample from black to gold[1]. The volume also decreases by ∼8% keeping the NaCl-type crystal structure. A long range-magnetic order occurs above 1.8 GPa[4, 5, 6]. Despite of extensive studies, the ground state of these phases and the mechanism of these two transitions are not fully understood. Moreover, it is uncertain whether the magnetically ordered state coexists with intermediate or trivalent Sm valence.

The nuclear magnetic resonance experiment (NMR) can be useful for microscopically investigating the magnetic properties and the energy gap. However, this experiment on SmS has not been carried out yet up to now. In the study of lanthnoide compounds, NMR experiments have usually been performed through ligand nuclei. But generally, sulfur is not suitable for NMR experiment owing to the extremely low abundance of the NMR-active isotope ^{33}S (0.76%) and the small value of nuclear gyromagnetic ratio of it($\gamma_N/2\pi$=3.2717 MHz/T). Then the NMR signal of sulfur nucleus was only observed in liquid solution. We prepared the ^{33}S isotope enriched SmS and succeeded in ^{33}S NMR experiment of black phase of SmS for the first time. In this paper, we present the results of the first ^{33}S-NMR measurement on SmS at ambient pressure.

2. Experimental

A powder sample of 98 at.% ^{33}S enriched SmS has been prepared via a two-step reaction of samarium metal and sulfur. First, stoichiometric amount of the starting materials was heated up to 900°C in a quartz ampoule. The reacted precursor was then fused in a tungsten crucible and heated up to 2000° in an radio-frequency (rf) induction furnace. The powder X-ray diffraction result on the obtained black ingot indicates the formation of cubic SmS with a trace amount of the secondary phase. The NMR experiment was carried out using a wide-band phase-coherent pulsed spectrometer. The ^{33}S NMR spectra were obtained using $\pi/2$-τ-π sequence with typical $\pi/2$ pulse length $\sim$15 μs and separation $\tau \sim 200$ μs.

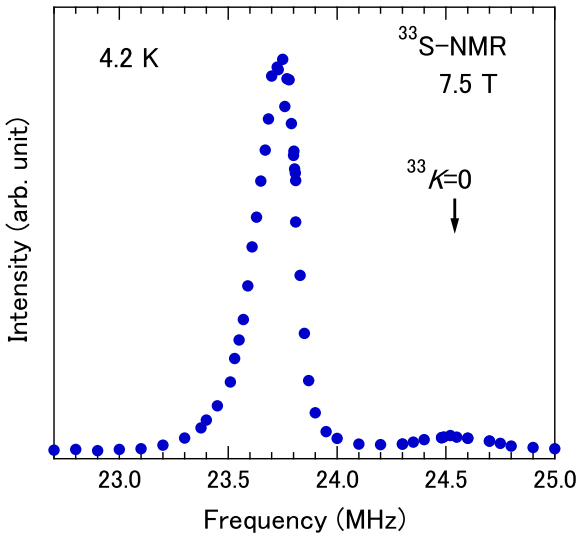

Figure 1. (Color online) ^{33}S NMR spectra at 4.2 K and 7.5 T. Data were taken by changing the frequency and recording the integrated spin-echo intensity.

3. Results and Discussion

Figure 1 shows the powder spectrum of ^{33}S (I=3/2) of SmS measured at 4.2 K and the magnetic field of 7.5 T. The full width at half maximum (FWHM) of this spectrum is about 220 kHz. We observed the ^{33}S NMR signal at lower frequency than at zero-Knight shift position (^{33}K=0 is 24.53 MHz), indicating the presence of a negative Knight shift. We checked the width of the spectra at various temperatures and found that the width increased with decreasing temperature, which corresponded to the increase in the shift from ^{33}K=0 position. Therefore, the width is mainly due to the distribution of the transferred hyperfine field induced by local lattice distortion around S site. We also observed the small signal at around 24.5 MHz being ascribed to the secondary phase in the sample. Since this signal was well-separated from the intrinsic one, we could perform the NMR measurement of SmS free of the influence of the secondary phase. As temperature is raised, the spectrum shifts to lower frequency and becomes weakly temperature dependent below 50 K. Generally the temperature dependence of the peak positions in NMR spectrum associates with that of the magnetic susceptibility. Then this behavior is explained by Van Vleck paramagnetism for nonmagnetic ground state of Sm^{2+} ion[3, 7, 8].

We performed the nuclear spin-lattice relaxation time (T_1) measurement, which was sensitive to the low-energy excitations. The nuclear magnetization $M(t)$ was obtained by the recovery of the spin-echo intensity. The nuclear magnetization recovery $m(t)$ after saturation comb pulses, which is defined by $m(t) = [M(\infty) - M(t)]/M(\infty)$, does not follow the single exponential function, as expected for nuclei in cubic symmetry. This is probably due to the distribution of T_1 in the sample caused by the local distortion of the lattice. We extracted $1/T_1$ by fitted the

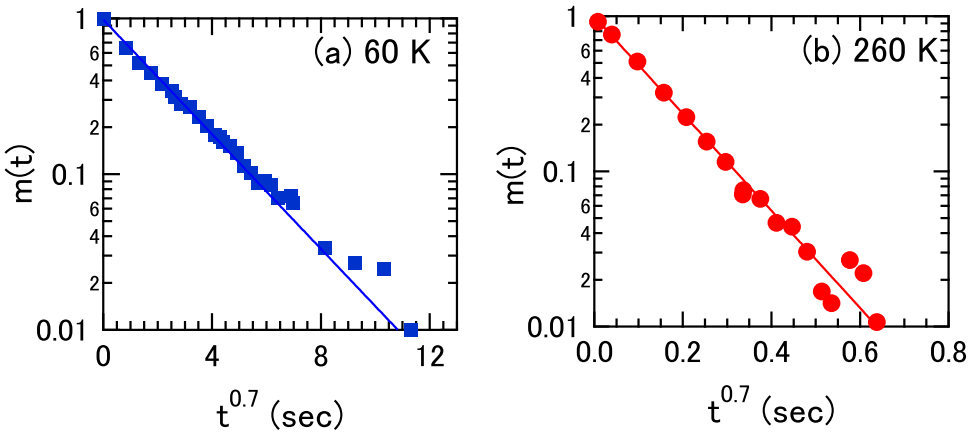

Figure 2. (Color online) The nuclear magnetization recovery, $m(t) = [M(\infty) - M(t)]/M(\infty)$ plotted against $t^{0.7}$ measured at (a) 60 K and (b) 260 K. The straight lines are the results of fitting.

recovery curves to a stretched exponential function,

$$m(t) = \exp\Big[-\Big(\frac{t}{T_1}\Big)^{\beta}\Big], \tag{1}$$

where β was the stretching exponent with $0 < \beta \leq 1$[9]. The obtained β is almost temperature-independent of about 0.7 in the experimental temperature range. This is shown by the straight line in the semilog plots between $m(t)$ and $t^{0.7}$ in Fig 2, indicating that the characteristic of $m(t)$ does not vary with temperature. Then we evaluated T_1 value by fitted the recovery curves with fixed β=0.7.

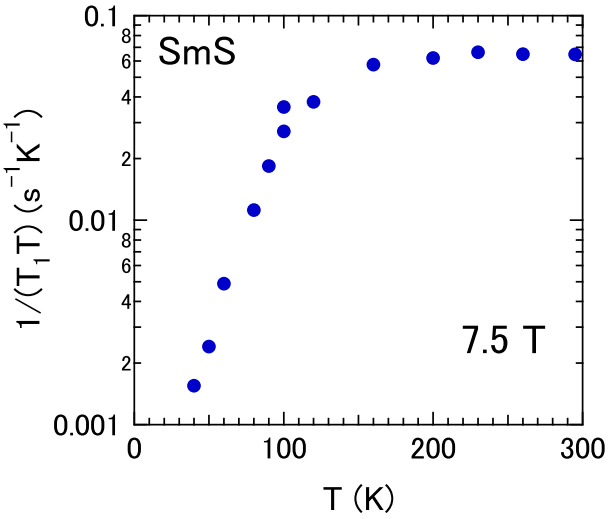

Figure 3. (Color online) Temperature dependence of $1/T_1$ at 7.5 T. T_1 values were derived using the stretched exponential function $m(t) = \exp[-(t/T_1)^{0.7}]$.

Figure 3 shows the temperature dependence of $1/(T_1T)$ measured at 7.5 T. $1/(T_1T)$ decreases rapidly with temperature. The data plotted T_1 vs $1/T$ (Arrhenius plot) yield a straight line as shown in Fig. 4, suggesting the presence of an excitation gap in the density of states at the Fermi level. The activation energy $\Delta/k_{\rm B}$ can be evaluated to be about 625 K from an Arrhenius plot of T_1 as shown in Fig. 4. This activation would correspond to a gap if the Fermi level lay

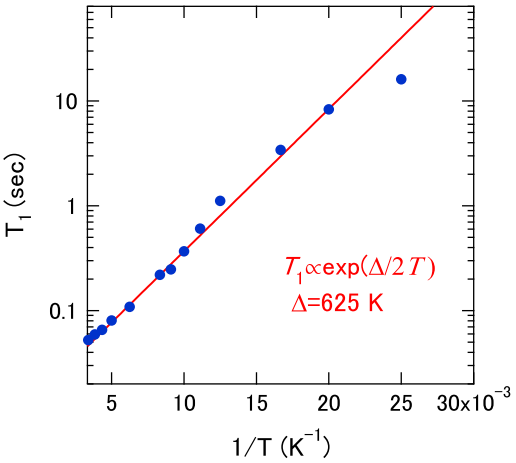

Figure 4. (Color online) T_1 vs $1/T$ plot. Δ/k_{B} was estimated to be about 625 K from the exponential behavior indicated by the solid line.

symmetrically within the gap. The value is comparable to the one estimated from the resistivity measurements[2, 3]. The sample dependence of electrical resistivity for SmS was intensively studied using single crystal samples and the size of Δ varied from 850 to 1600 K depending on samples[3]. Moreover, Δ is monotonically reduced by increasing external magnetic field[3]. We performed NMR experiment in the magnetic field of 7.5 T using the powdered sample of SmS. Therefore, the difference in Δ between the previous report and the present study possibly attributes to sample dependence and magnetic field effect. In order to understand the pressure induced insulator-metal transition of SmS, the NMR measurement under pressure is in progress.

4. Summary

We have prepared the ^{33}S isotope enriched SmS and investigated it by the NMR experiment at ambient pressure. The ^{33}S NMR signal was successfully obtained, and, with lowering temperature, shifted largely to lower frequency and became weak temperature dependent below 50 K. This behavior is ascribable to the Van Vleck paramagnetism of nonmagnetic Sm^{3+} ion. $1/T_1$ decreases rapidly, with activated temperature dependence and the activation energy was evaluated to be 625 K from an Arrhenius plot of $1/T_1$. Therefore, the presence of an excitation gap in SmS at ambient pressure was microscopically established.

Acknowledgments

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