NMR of ^{93}Nb perturbed by Quadrupole Interaction in Quasi-One-Dimensional $BaNbS_{3+d}$

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Field-swept NMR spectra of ^{93}Nb are examined for a sample of $BaNbS_{2.96}$ which has a semiconductive temperature dependence of the resistivity at low temperature, and a sample of $BaNbS_{3.03}$ which has a metallic temperature dependence at low temperature. Both spectra are so-called NMR powder patterns perturbed by a quadrupole interaction with a quadrupole frequency $\nu_Q = 3e^2qQ/2I(2I-1)h$ of 2.5 [MHz]. No appreciable difference in the spectra has been observed between the two samples, suggesting that the amplitude of the conduction electron density is too small to perturb the electronic environments around the niobium atoms. The general behavior of the nuclear spin-lattice relaxation of ^{93}Nb in both compounds is consistent with an interpretation that the relaxation at low temperature is dominated by a Korringa mechanism and at higher temperature by a quadrupole interaction.

Key words: NMR; ^{93}Nb; $BaNbS_3$; Quadrupole Interaction.

1. Introduction

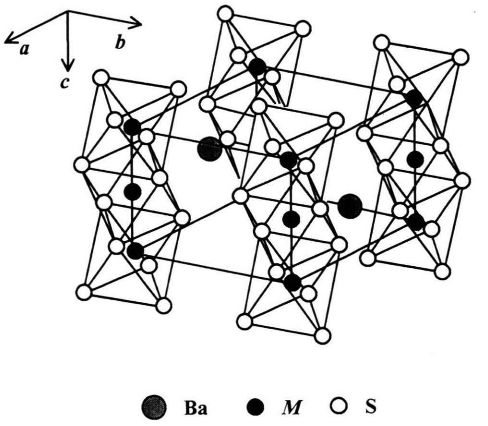

Fig. 1. The crystal structure of $BaNbS_3$.

The sulfide $BaNbS_3$ has a hexagonal $BaNiO_3$ structure with space group $P6_3/mmc$ at room temperature [1, 2]. The niobium atoms are surrounded by face sharing sulfur octahedra and form linear chains parallel to the c-axis, as shown in Figure 1. The isostructural $BaVS_3$ shows interesting metal-insulator-magnetic transitions with decreasing temperature [3, 4]. It has recently been shown that the temperature dependence of the electrical resistivity of $BaNbS_3$ is very sensitive to its stoichiometry [5]. Single-phase specimens of $BaNbS_{3+d}$ ($2.93 < 3 + d < 3.06$) were prepared by the sulfurization method using CS_2 [5]. The lattice constants a and c are little sensitive to the value of d in the region $-0.07 < 3 + d < 3.06$. $BaNbS_{2.93}$ indicates a semiconductor-to-semiconductor gradual transition around 100 K, while $BaNbS_{3+d}$ ($2.96 < 3 + d < 3.06$) shows a hump-shaped anomalous behaviors in the resistivity [5]. However, no anomaly in the magnetic susceptibility has been observed. The magnetic susceptibility is nearly temperature independent with an extremely small Curie-like increase at low temperatures [5]. No structural transition was observed, including the temperature range where the hump-shaped anomaly in the resistivity was observed [5]. A

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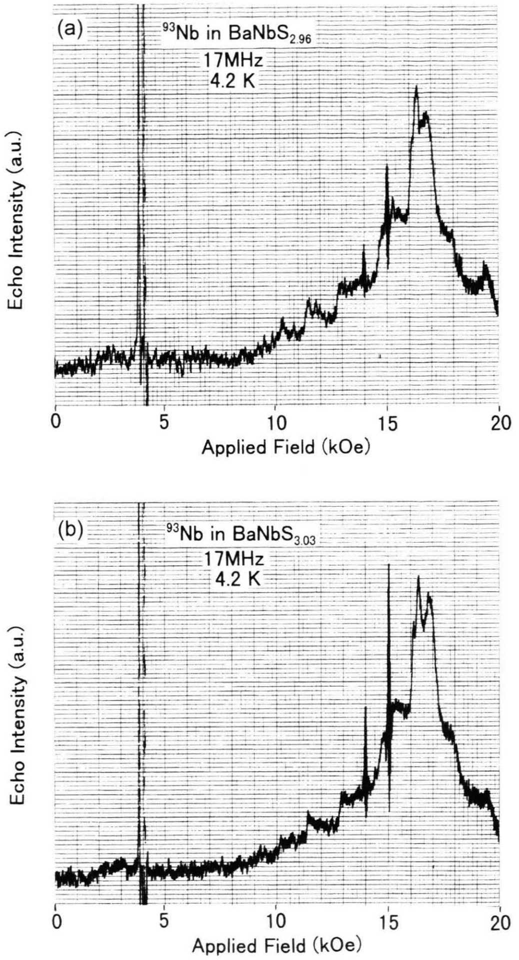

Fig. 2. Boxcar traces of field-swept spin-echo spectra of ^{93}Nb in BaNbS$_{2.96}$ (a), and BaNbS$_{3.03}$ (b), taken at an operating frequency of 17 MHz at 4.2 K.

purpose of the present NMR experiment is to elucidate the electronic state in BaNbS$_{3+d}$ from a microscopic point of view by doing NMR experiments of ^{93}Nb, since the quadrupole interaction of ^{93}Nb ($I = 9/2$, $Q = -0.2$ barn) is expected to strongly disturb a field-swept NMR spectrum if the local symmetry around the Nb atoms is changed by the stoichiometry.

2. Field-swept NMR Spectra of ^{93}Nb

Two samples were chosen and prepared by the sulfurization method using CS$_2$ as described in the previous report; (a) BaNbS$_{2.96}$, which has a semiconductive temperature dependence of the resistivity at low temperatures and (b) BaNbS$_{3.03}$, which has a metallic temperature dependence at low temperatures [5]. NMR experiments have been performed between 4.2 and 100 K with a home-built, phase coherent pulsed NMR spectrometer. Field-swept NMR spectra of ^{93}Nb were examined for two samples (a) and (b). Examples of spectra at 4.2 K and an operating frequency of 17 MHz are shown in Fig. 2 (a) and (b), respectively. Both spectra are so-called NMR powder patterns perturbed by a quadrupole interaction. Free decay wiggles caused by ^{1}H from glue, ^{19}F from teflon, ^{65}Cu and ^{63}Cu from NMR coil should be neglected. A weak and sharp extrinsic signal seems to be overlapped at the peak position of each spectrum; the intensity is estimated to be less than 0.4% of the total intensity. The quadrupole frequency, $\nu_Q = 3e^2qQ/2I(2I-1)h$ is estimated to be 2.5 MHz. A distribution in the quadrupole frequency with a standard deviation of 0.1 ν_Q assuming a Gaussian distribution explain the slightly broadened spectra observed. However, no appreciable difference in the spectra (a) and (b) is observed. This suggests that the local symmetry around the niobium atoms does not change for a majority number of niobium sites. Probably, the amplitude of the conduction electron density is too small to perturb the electronic environments around the niobium atoms.

3. Nuclear Spin-lattice Relaxation

The nuclear spin-lattice relaxation behavior of ^{93}Nb in BaNbS$_{2.96}$ and BaNbS$_{3.03}$ has been examined by observing the recovery of the nuclear magnetization $M(t)$ after a time t from a saturating rf comb to the thermal equilibrium magnetization M_0 at 17 MHz. An example of the data at 4.2 K for ^{93}Nb in BaNbS$_{2.96}$ is shown in Figure 3. The signal was not saturated completely, but recovered with a very short time constant. This seems to be partly due to a spin diffusion in a spectral space, because we are digging a small hole by the rf pulse in a wide spectrum shown in Fig. 2, and partly due to the relaxation in a multi-level NMR system perturbed by a quadrupole interaction of ^{93}Nb with $I = 9/2$. After the fast recovery of the nuclear magnetization, the recovery is reasonably well described by a single exponential function at least in a decade, as is seen in Figure 3. We assume that this longer time constant is the nuclear spin lattice relaxation time T_1. The temperature dependence of the nuclear spin-lattice relaxation rate T_1^{-1} of ^{93}Nb in BaNbS$_{2.96}$ and BaNbS$_{3.03}$ is plotted in Figure 4.

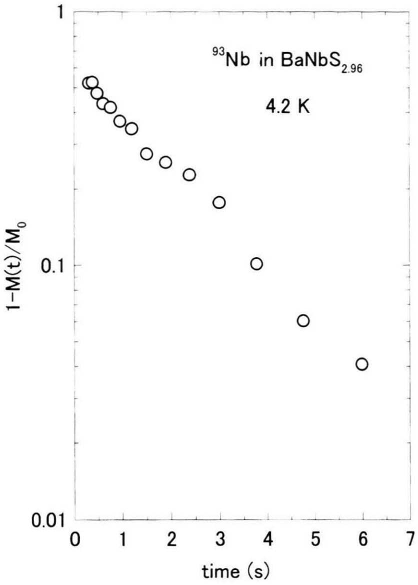

Fig. 3. Behavior of the saturation recovery of the nuclear magnetization of ^{93}Nb in BaNbS$_{2.96}$ at 4.2 K and 17 MHz.

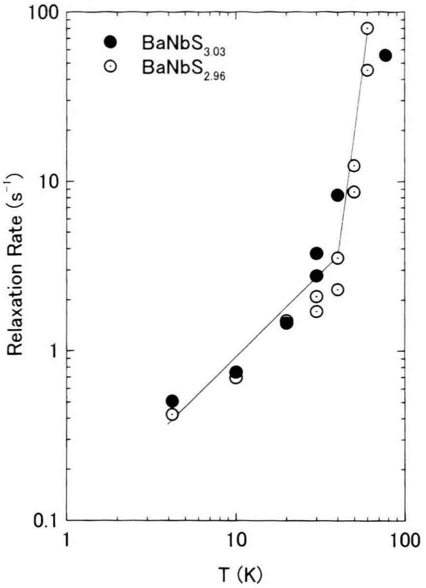

Fig. 4. Temperature dependence of the nuclear spin-lattice relaxation rate of ^{93}Nb in BaNbS$_{2.96}$ (open circles), and BaNbS$_{3.03}$ (closed circle), taken at an operating frequency of 17 MHz.

Unfortunately, errors are large because of the complex recovery of the nuclear magnetization and the weakness of the signal due to very broad width seen in Fig. 2, and no detectable difference in the relaxation rates is observed for BaNbS$_{2.96}$ and BaNbS$_{3.03}$. However, the following features are seen in Figure 4. The relaxation rate has a strong temperature dependence above 30 K, and has a weak temperature dependence in the temperature range from 4 to 30 K. Considering the negligible magnetic impurities in this system derived from the static susceptibility data [5], the weak temperature dependence of the relaxation rates in the low temperature region can be assigned to the Korringa mechanism with $(T_1T)^{-1} = 0.09$ (sec K)$^{-1}$. This value is about 3 % of $(T_1T)^{-1} = 2.8$ (sec K)$^{-1}$ for the case of niobium metal, suggesting that the density of states of the conduction band is about 1/5 of that of niobium metal. The strong temperature dependence above 30 K is consistent with a relaxation mechanism due to a fluctuation of the local field gradient at niobium sites with $T_1{}^{-1} = aT^7$.

In summary, the major features of the NMR spectra and nuclear spin-lattice relaxation rates of ^{93}Nb in BaNbS$_{2.96}$ and BaNbS$_{3.03}$ are found to be similar, suggesting that the resistivity anomaly observed is due to a small difference in the conduction band in this system.

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