

⁹³Nb Nuclear Spin-Spin Relaxation in the Low-Dimensional Antiferromagnet Fe_{0.25}NbS₂

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⁹³Nb nuclear spin-spin relaxation has been examined in the low-dimensional antiferromagnet Fe_{0.25}NbS₂ between 4.2 K and 300 K. The relaxation is characterized by two T_2 's. The temperature dependence is discussed together with the origin of the disappearance of the fast decay at low temperatures.

Key words: NMR; T_2 ; Spin Dynamics; Fe_{0.25}NbS₂; Antiferromagnetism.

1. Introduction

Spin dynamics is one of the main interests in modern material science. Unusual behaviours are expected in low-dimensional magnets. Disulfides and diselenides of niobium and tantalum intercalate the first-row transition metal atoms to form low-dimensional magnets. Though many studies were made on the physical properties of these magnets [1], they were confined within macroscopic ones. The spin dynamics in these dichalcogenides have been studied in a spin glass [2], but have not been studied in low-dimensional magnets. The purpose of the present study is to obtain dynamical information about one of them, Fe_{0.25}NbS₂, by ⁹³Nb NMR. Of the intercalation compound of NbS₂ with Fe, two compositions are known, Fe_{0.25}NbS₂ ($P6_3/mmc$) and Fe_{0.33}NbS₂ ($P6_322$). The former shows antiferromagnetism below 137 K, and the latter below 47 K [1].

2. Experimental

The compound Fe_{0.25}NbS₂ was synthesized by the method described in [1]. The product was ground, and the particles under 63 μ in size were used as the sample. For comparison, samples of Fe_{0.33}NbS₂, 2H-NbS₂, and 2H-NbSe₂ were prepared in a similar way. The structures were confirmed by X-ray diffraction analysis.

The ⁹³Nb spin echoes, following $\pi/2 - \tau - \pi$ pulse sequences, were examined in a field of 4.7079 T. The width of the $\pi/2$ pulse was 2 μ s, typically. The spec-

trum was obtained as frequency dependence of the echo intensity with the apparatus tuned at every frequency. Though for NbSe₂ a pattern compatible with the one obtained by field sweep [3] was obtained, the spectral data are used only for qualitative discussion, because the sensitivity of the apparatus was not calibrated.

Because the nuclear spin-lattice relaxation was too fast to saturate the resonance line, the spin-spin relaxation was instead examined. The spin-spin relaxation time T_2 was determined from the decay of the echo intensity at the frequency where the intensity was largest. The dead time of the apparatus was about 40 μ s. The temperature was regulated within 0.1 K, but the exactness of the measurement was within ± 0.3 K. In the following, “77 K” and “300 K” mean liquid nitrogen and room temperatures, respectively.

3. Results and Discussion

3.1. Knight Shift and EFG

Figure 1 shows the ⁹³Nb spectra of Fe_xNbS₂ ($x = 0, 0.25$, and 0.33). For non-zero x the satellites seem to escape from the observation. Also at 4.2 K the pattern for $x = 0.25$ showed a similar breadth but extended toward the higher frequency side at 300 K. Around 137 K the pattern exhibited a somewhat complicated change. The signal intensity changed in proportion to the inverse of the temperature T , also for $x = 0.25$ without enhancement.

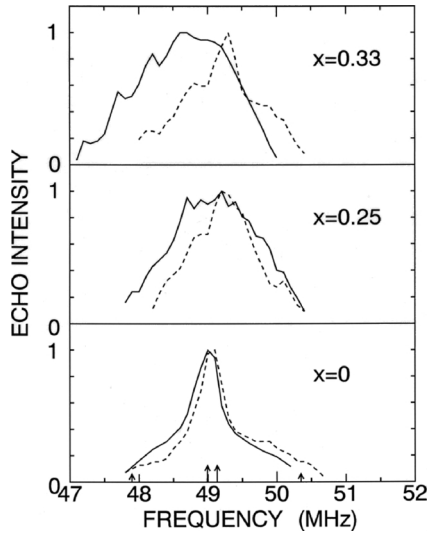


Fig. 1. ^{93}Nb spectra of Fe_xNbS_2 ($x = 0, 0.25, 0.33$) at 77 K (solid lines) and 300 K (broken lines). They were obtained at $t = 80 \mu\text{s}$ for $x = 0$ and at $t = 52 \mu\text{s}$ for $x = 0.25$ and $x = 0.33$. The echo intensities are normalized at the peaks. At the bottom, the long arrows indicate the positions of the divergences of the central transition ($-1/2 \leftrightarrow +1/2$) and the short ones indicate those of the satellite ones ($+1/2 \leftrightarrow +3/2$, $-1/2 \leftrightarrow -3/2$) with values of $e^2qQ = 59 \text{ MHz}$ and $K_{\perp} = -0.1\%$ at 77 K [6] and $K_{\parallel} = 0\%$.

Fe atoms, on intercalation into NbS_2 , occupy octahedral sites surrounded by six S atoms in the 2H structure (space group $P6_3/m$). In both compounds ($x = 0.25$ and 0.33) there are two kinds of sites for Nb atoms, one adjacent to Fe atoms along the c -axis (site A) and one not adjacent (site B). Since each transition is considered to consist of two components corresponding to these sites, with different Knight shifts, K 's, and quadrupole coupling constants, e^2qQ 's, it is difficult to determine their magnitudes separately. For non-zero x at 300 K, however, Fig. 1 indicates positive increases of the K 's and of the e^2qQ 's in the absolute value accompanying the intercalation. In the $x = 0.25$ composition the symmetry at site B falls from C_6 to C_2 on intercalation, and consequently the asymmetry parameter η recovers from zero. This should cause a significant change in the pattern [4]. However, since a large broadening is observed also for the $x = 0.33$ composition, retaining its vanishing η on intercalation, the broadening still indicates increases of the e^2qQ 's. The increase of e^2qQ averaged between the sites amounts to a factor of two for both compounds.

Most of the physical properties of these compounds have been successfully interpreted using the rigid band

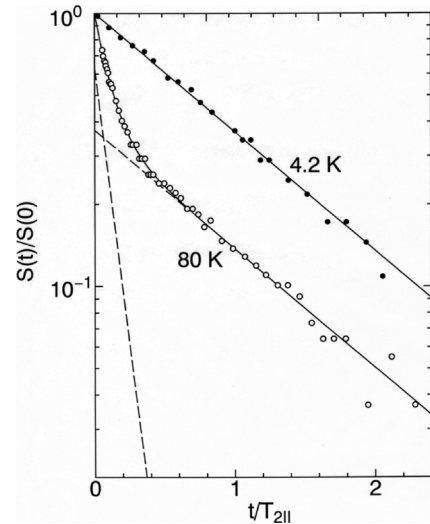


Fig. 2. Decay curve of the ^{93}Nb spin echo of $\text{Fe}_{0.25}\text{NbS}_2$. The broken lines represent the contributions of two components at 80 K. The abscissa is normalized by the respective values of $T_{2\text{II}}$ ($3220 \mu\text{s}$ at 4.2 K and $657 \mu\text{s}$ at 80 K). The value of $T_{2\text{I}}$ at 80 K is $70 \mu\text{s}$.

model [1]. The lower d-band is half-filled and the Fermi level, ϵ_F , is near the sharp peak of the density of states, $N(\epsilon)$. Since, on intercalation into NbS_2 , Fe atoms are considered to be double-charged, the number of electrons in this band increases from 1 in $x = 0$ to $3/2$ in $x = 0.25$ and to $5/3$ in $x = 0.33$ compositions, resulting in a decrease of $N(\epsilon_F)$. Moreover, since it is reported for Fe_xNbS_2 ($x = 0.25, 0.33$) that the band broadens on intercalation [1], $N(\epsilon_F)$ is expected to decrease still more. Then, the positive shifts of the patterns at 300 K accompanying the intercalation are explained as a decrease of the negative Knight shift due to the core polarization, as in the case of the intercalation of the pyridine molecule [5]. The increase of $|q|$ can be explained similarly, if the positive contribution from the valence band is considered to be overwhelmed by the negative one from the conduction band, because the transfer of more charges occurs than in the intercalation of pyridine [6]. The further broadening at low temperatures in non-zero x compounds may be related with the magnetism.

3.2. Spin-Spin Relaxation

Examples of the decay of the echo intensity are shown in Figure 2. The decay was double-exponential above 20 K in $\text{Fe}_{0.25}\text{NbS}_2$ and at 77 K and 300 K in $\text{Fe}_{0.33}\text{NbS}_2$. Thus the echo intensity $S(t)$ at time t ,

measured from the leading edge of the first pulse, was fitted, for non-zero x , by the relaxation function

$$\frac{S(t)}{S(0)} = w_I \exp\left(-\frac{t}{T_{2I}}\right) + w_{II} \exp\left(-\frac{t}{T_{2II}}\right), \quad (1)$$

$$w_I + w_{II} = 1, \quad (2)$$

where the first term corresponds to the fast decay and the second to the slow one, and w_I and w_{II} represent their fractional weights. In NbS_2 and NbSe_2 , on the other hand, the decay was single-exponential at all temperatures examined. Since in the latter compounds there is only one kind of sites for Nb atoms, the double-exponential decays in non-zero x compounds are attributed to the existence of two sites. For the $x = 0.25$ composition, w_I was nearly constant and took values of $0.7 \sim 0.8$ down to 150 K. For the $x = 0.33$ composition, w_I was $0.6 \sim 0.7$ both at 77 K and 300 K. The values of w_I at temperatures higher than the Néel point T_N are close to the fractional abundance of Nb atoms, at site B, $3/4$, if $x = 0.25$, and that at site A, $2/3$, if $x = 0.33$. Therefore, the component I is assigned to site B if $x = 0.25$ and to site A if $x = 0.33$. However, w_I in the $x = 0.25$ composition dropped down to 0.5 centering 137 K between 150 K and 100 K, and once recovered up to 0.7. From 70 K it rapidly decreased, and below 20 K the initial decay almost disappeared, as seen in Figure 2.

Taking advantage of the difference in the patterns observed at $t = (2 \sim 3) \cdot T_{2I}$ and $t \lesssim T_{2I}$, the separation of the spectrum was attempted for $\text{Fe}_{0.25}\text{NbS}_2$. As a result, it was found that at 77 K component I had the center of gravity at a 0.4 MHz higher frequency than component II. This is in accordance with the observation that w_I was larger by 15% at the higher frequency side within the spectrum. Around 137 K, however, only a result suggesting a splitting of the peak was obtained. For the complete separation of the spectra, the observation of the relaxation function at each frequency [7] may be required.

3.3. Temperature Dependence of T_2

The temperature dependence of the spin-spin relaxation rate $1/T_2$ of Fe_xNbS_2 is shown in Figure 3. $1/T_2$ of NbSe_2 showed a linear temperature dependence.

Though it is not difficult to measure T_2 without ambiguity, the interpretation is not so straightforward as that of the spin-lattice relaxation time T_1 . In case of magnetic relaxation, $1/T_2$ is generally expressed as

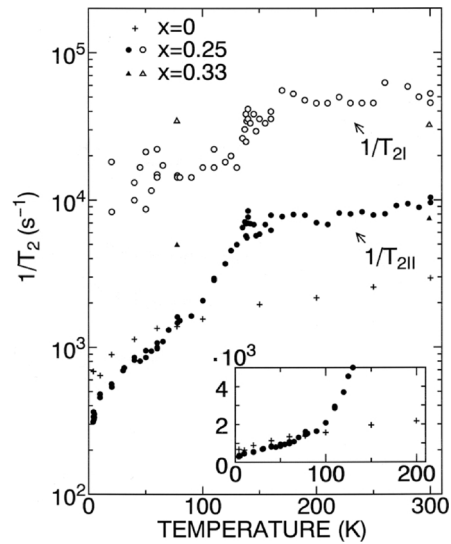


Fig. 3. Temperature dependence of the ^{93}Nb nuclear spin-spin relaxation rate $1/T_2$ of Fe_xNbS_2 ($x = 0, 0.25, 0.33$). For $x = 0.25$ the values of $1/T_{2I}$ corresponding to some values of $1/T_{2II}$ are not shown because of the low accuracy.

the sum of secular and non-secular parts. The former part is the static component of the correlation function for the component $\mathbf{H}(t)_{||}$, parallel to the quantization axis, of the time-dependent magnetic field $\mathbf{H}(t)$. The latter part is the Larmor frequency component of the correlation function for the perpendicular component $\mathbf{H}(t)_{\perp}$, and $1/T_1$ is equal to twice this part [8]. When the energy levels are unequally spaced by the quadrupolar interaction, the spin-lattice relaxation is multi-exponential [9], and the largest time constant is T_1 . Furthermore, if the fluctuations of $\mathbf{H}(t)$ are isotropic and if the condition $\omega\tau_c \ll 1$ is satisfied for the correlation time τ_c and the Larmor frequency ω , T_2 is related with T_1 by the equation [10]

$$\frac{1}{T_2} = \left(I + \frac{1}{2}\right)^2 \frac{1}{T_1}. \quad (3)$$

The spin-lattice relaxation in metals is governed mainly by the interactions with conduction electrons, and $1/T_1$ is proportional to T . In NbS_2 and NbSe_2 the dominant interactions for the relaxation are known to be magnetic [11]. Thus $1/T_2$ is analyzed by the equation

$$\frac{1}{T_2} = a + bT + f(T), \quad (4)$$

where a is the contribution from the nuclear dipole-dipole interaction and b is $(I + 1/2)^2$ divided by the

Table 1. Experimental values of a and b , and the calculated values of $\sqrt{\langle\Delta\omega^2\rangle}$.

Compound	a (10^2 s ⁻¹)	b (s ⁻¹ K ⁻¹)	$\sqrt{\langle\Delta\omega^2\rangle}$ (10^4 s ⁻¹)
NbS ₂	7.6	7.4 ^a	1.25
NbSe ₂	7.0 ^b	51 ^{b,c}	1.10
Fe _{0.25} NbS ₂	(I) 100 ~ 130	50 ~ 60	1.22
	(II) 3.1	12	

^a The use of this value in the relation $b = (I + 1/2)^2 / TT_1$ yields $T_1T = 3.4$ s · K, which is much larger than the value $T_1T = 0.5$ s · K [5].

^{b,c} These values are compatible with the values $T_2 = 1.12$ ms at 1.3 K [11] and $T_1T = 0.45$ s · K [5].

constant for T_1T . $f(T)$ represents the contribution from fluctuations of the moments in magnetic metals and is expected to show some anomalies at the critical temperature and a rapid decrease at low temperatures.

In Table 1 the experimental values of a and b , and the values of the square root of the second moment, $\sqrt{\langle\Delta\omega^2\rangle}$, calculated for the direct dipole-dipole interaction among like spins are listed [8]. When the line is inhomogeneously broadened, the spin flip-flop is suppressed, and this contribution is reduced roughly by a factor of the ratio of the homogeneous width to the inhomogeneous one. For the non-magnetic metals NbS₂ and NbSe₂, however, when the inhomogeneous broadenings, of an order of 10^7 s⁻¹, are taken into account, the values of $\sqrt{\langle\Delta\omega^2\rangle}$ are too small to explain the values of a . Indirect coupling seems to work also. The large difference in the values of b between them may be due to some differences in $N(\epsilon_F)$ and the strength of interactions.

In the magnetic metal Fe_{0.25}NbS₂ the values of a and b for component II are obtained from the asymptote of $1/T_{2II}$ to 0 K, as shown in the inset of Figure 3. The value of a is different from that for NbS₂ in spite of the close values of $\sqrt{\langle\Delta\omega^2\rangle}$. This is considered to be due to the increase of the inhomogeneous broadening. According to the rigid band model, on the other hand, $N(\epsilon_F)$ decreases accompanying the intercalation, and consequently b is expected to be smaller than for NbS₂. Though the value of b for component II is somewhat larger than for NbS₂, this does not necessarily conflict with the expectation, since the value gives only the upper limit. In contrast with component II, the value of a in component I is more than one order of magnitude larger. Since the dipole-dipole interaction is common and the inhomogeneous broadenings are not much different, a is not considered to be so much different between the two components. Similarly, since $N(\epsilon_F)$ and the electron-nucleus interactions are common between

Table 2. Calculated values for the squared fluctuation $(\delta H_{\text{dip}})^2$ of the dipole field and the experimental values of $(1/T_2)_{300\text{K}}$.

Compound	Site	$(\delta H_{\text{dip}})^2$ ($\mu^2 \cdot 10^{-4} \text{A}^{-6}$)	$(1/T_2)_{300\text{K}}$ (10^4 s ⁻¹)
Fe _{0.25} NbS ₂	A	8.0	1.0
	B	87	4.9
Fe _{0.33} NbS ₂	A	106	3.2
	B	46	0.74

the two sites, b is also considered to be common. Nevertheless, the value of b for component I is also too large, though it includes large errors. These discrepancies suggest that the large value of $1/T_{2I}$ at low temperatures should be attributed not to the first two terms in (4) but rather to $f(T)$ for component I.

3.4. Relation of T_2 with the Magnetic Structure

Usually, fluctuations of the magnetic field are expected to be large near magnetic moments. As for the $x = 0.25$ composition, nevertheless, the smaller $1/T_2$ was assigned to the site closer to Fe atoms (site A). This can be understood by considering the difference in the magnetic structures: Site A in Fe_{0.25}NbS₂ is sandwiched by Fe atoms from above and below, while site A in Fe_{0.33}NbS₂ has one Fe atom as neighbour only on one side. Among the Fe spins, the RKKY and the super-exchange interactions work, in addition to the interaction through the empty Nb orbitals. As a result, in the ordered state of Fe_{0.25}NbS₂, the Fe spins are considered to be aligned antiparallel to each other along the c -axis and parallel within the c -plane [1]. In Fe_{0.33}NbS₂ the spins are antiferromagnetic both between and within the planes, and the ordering has the wurtzite form of β -MnS (the third kind ordering) [12].

In order to examine the fluctuations concretely, as an excitation mode the reversal of the spins in an Fe chain along the c -axis is supposed in the former compound, and the reversed one within an adjacent Fe plane is supposed in the latter. When the dipole field at Nb sites produced by the magnetic moment μ of Fe spins is considered, it is noted that in the excited state of the $x = 0.25$ composition the lateral contributions from the reversed Fe spins above and below the adjacent A sites no longer cancel but strengthen each other. Besides, within the plane the Nb-Fe distance is much smaller at site B than at site A. Table 2 shows the results of a calculation for the squared fluctuation of the dipole field, $(\delta H_{\text{dip}})^2$, between the ground and the excited states. Though $(\delta H_{\text{dip}})^2$ is proportional to $f(T)$, it is com-

pared directly with $1/T_2$, because the contribution of $a + bT$ is relatively small even at 300 K. A calculation was made to the second nearest neighbours when the contribution from the first nearest ones vanishes. The results are consistent with the ratios of the observed $1/T_2$ at 300 K between two sites in both compounds.

When a field $\mathbf{H}_{\text{exch}}$ due to an exchange type interaction $\mathbf{AI} \cdot \mathbf{S}$ with the nuclear spin $\mathbf{I}$ at the position $\mathbf{r}$ with respect to the Fe spin $\mathbf{S}$ is instead considered, if $x = 0.25$ it is cancelled at both sites even in the excited state, and if $x = 0.33$ the dependence of A on r must be known in advance to the calculation. Reversely, when the interaction is isotropic and fluctuations of spins are approximated as the Gaussian type, A can be determined using the relation [13]

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{\sqrt{\pi} S(S+1) A^2}{3\hbar^2 \omega_e}, \quad (5)$$

where ω_e is written with the exchange interaction energy J and the number of nearest neighbours z as

$$\omega_e^2 = \frac{2J^2 z S(S+1)}{3\hbar^2}. \quad (6)$$

For $1/T_2$ the values at 300 K are used with subtraction of the contributions of $a + bT$ for site II, in common for both sites. When the relation

$$T_N = \frac{2S(S+1)J}{3k} \quad (7)$$

is used to obtain the value of J , (5) yields values of $1.7 \cdot 10^{-19}$ erg and $5.1 \cdot 10^{-19}$ erg for A's at site A and site B, respectively.

3.5. Nature of Spin Fluctuations

The nuclear spin is quantized along the static field $\mathbf{H}_0$, while $\mathbf{H}(t)$ is produced by Fe spins aligned with respect to the c -axis. This yields a problem related to the low-dimensionality: When $\mathbf{H}(t)$ is the dipole field $\mathbf{H}_{\text{dip}}$, proportional to $\mathbf{S} - 3\mathbf{S}(\mathbf{S} \cdot \mathbf{r})/r^2$, the direction is distributed with an angle θ from $\mathbf{H}_0$ in the powder sample, with the weight $\sin \theta$. Then, both $\mathbf{H}(t)_{\parallel}$ and $\mathbf{H}(t)_{\perp}$ depend on θ . Consequently, $1/T_1$ and $1/T_2$ of each crystal grain have θ dependences, and the relaxation function will be an integral of the exponent depending on θ , weighted with $\sin \theta$. This conflicts with the observation. Since $\mathbf{H}_{\text{dip}}$ depends on the direction of $\mathbf{r}$, the same problem remains even when $\mathbf{H}_0$ is larger than the spin flipping field or the critical field, and

even when the temperature is higher than T_N , where the Fe spins are isotropic. However, once the condition $\omega\tau_c \ll 1$ is satisfied, the θ dependences of the secular and non-secular parts disappear together in the sum, and a single-exponential behaviour per site results for the spin-spin relaxation, though the θ dependence still remains for the spin-lattice relaxation. Also in case of the exchange field, $\mathbf{H}(t)$ is not isotropic because of the anisotropy of $\mathbf{S}$, so that the same problem occurs. However, when the condition $\omega\tau_c \ll 1$ is satisfied, a single-exponential spin-spin relaxation similarly results. Above T_N , $\mathbf{H}_{\text{exch}}$ is isotropic and this kind of problem does not occur. After all, the observation of single-exponent per site guarantees the condition for (3).

Next the origin of the disappearance of the fast decay below 20 K is considered. With a pulse of 2 μ s the whole spectrum of the resonance line is not observed at a time. If the respective spectra for the components relatively change the positions of their centers or breadths, w_I does not reflect their abundances correctly. The drop of w_I around 137 K may be related with the complicated change of the spectra. However, the disappearance of the fast decay cannot be explained by an escape of the observation, because such a degree of change in the pattern as observed at 4.2 K is insufficient. In the ground state the magnetic fields produced by Fe spins are cancelled at both sites, so that they are magnetically not different from each other. Figure 3 shows that for component II the contribution to $1/T_2$ from $f(T)$ becomes negligible below 70 K. Besides, it was suggested above that $f(T)$ for component I retains a large value at low temperatures. Therefore, the fact that the fast decay disappears without $1/T_{2I}$'s approaching $1/T_{2II}$ affords the following picture to the excitations: In advance to their progressive cessation toward 0 K, they localize in the time scale of the Larmor period and continue to produce a large fluctuating field concentratedly at a decreasing fraction of site B.

4. Conclusion

The present study revealed a variety of microscopic features, in particular spin dynamics, in the low-dimensional antiferromagnet Fe_{0.25}NbS₂. Two components in the relaxation curve were assigned to two sites of Nb atoms. This assignment is compatible with the reported magnetic ordering, at least for the dipolar interaction and the supposed excitation mode. The observed temperature dependence of T_2 was analyzed in

comparison with that in NbS_2 . The nature of the field at Nb sites produced by Fe spins is closely related with the low-dimensionality, but characterized by the fact of one exponential decay per site. A picture for the excitation was proposed from the disappearance of the fast decay at low temperatures. However, further investigation seems to be required in order to get the complete understanding of the spin dynamics.

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