Magnetic frustration effect in the multi-band vanadate NaV$_2$O$_4$

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Abstract. We have performed $^{23}$Na and $^{51}$V NMR measurements to study the magnetic frustration effect on the local magnetic properties of NaV$_2$O$_4$ with the double chain structure. In the paramagnetic state, we find the presence of the ferromagnetic interaction, which competes with the antiferromagnetic interaction, coming from the multi-band effect. The spin structure in the magnetically ordered state, an incommensurate helical structure which appears due to the competition between the magnetic interactions, is proposed. Thus the magnetic frustration closely related to the multi-band effect is concluded to play an essential role for the magnetic properties of NaV$_2$O$_4$.

1. Introduction

Mixed-valence vanadium oxides with geometrically frustrated lattice show fascinating physical phenomena such as heavy fermion behavior in LiV$_2$O$_4$ with the spinel structure [1]. Recently NaV$_2$O$_4$ with the mixed valence of V$^{3+}$:V$^{4+}$=1:1 has attracted attention as a candidate of the itinerant frustrated systems [2]. This vanadate crystallizes into the CaFe$_2$O$_4$ type structure which has a V$_8$O$_{16}$ framework composed of double chains of edge sharing V(1)O$_6$ or V(2)O$_6$ octahedra. Na atoms are located in a tunnel of the framework. Then the double chain structure is expected to have a low dimensional electronic structure with the geometrical frustration.

NaV$_2$O$_4$ exhibits metallic conductivity down to 40 mK, and a transition from the paramagnetic to antiferromagnetic (AFM) states occurs at $T_N$=140 K [2]. Above $T_N$, the presence of a ferromagnetic (FM) correlation was reported from the magnetic susceptibility measurement in spite of the AFM transition. However, the origin of the FM interaction has not been clarified. Below $T_N$, the AFM3 phase appears at low magnetic fields in the temperature $T$ versus magnetic field $H$ phase diagram which includes the AFM1 and AFM2 phases [3]. The spin structures in the AF phases remain controversial in spite of several experimental studies [2, 4, 5].

In this study, we have made $^{23}$Na and $^{51}$V NMR measurements to investigate the magnetic frustration effect on the local magnetic properties of NaV$_2$O$_4$. We confirm the presence of the FM correlation in the paramagnetic phase and discuss the origin of the FM interaction on the basis of the multi-band effect. An incommensurate helical spin structure, which comes from the competition between the FM and AFM interactions, in the AFM3 phase is proposed.
2. Experiments

Single crystals of NaV$_2$O$_4$ were prepared by the hydrothermal synthesis method in a high-pressure furnace [3]. A crystal of 0.5×1.0×1.5 mm$^3$ was used for present NMR measurements. $^{23}$Na and $^{51}$V Fourier-transformed (FT) NMR spectra were measured in a magnetic field of $H_0$=3.0 T and 5.8701 T by using a pulsed spectrometer. The $^{23}$Na Knight shift was determined as $K=(\nu_{\text{res}}-\nu_0)/\nu_0$ where $\nu_{\text{res}}$ and $\nu_0$ (=66.114 MHz) are $^{23}$Na resonance frequencies in the NaV$_2$O$_4$ sample and the aqueous NaVO$_3$ solution, respectively. Frequency-swept $^{51}$V NMR spectra at 4.2 K were taken point by point in zero external field.

3. Results and discussion

Figure 1 shows the $T$ dependence of the $^{23}$Na Knight shift $^{23}K$ determined from the peak position in the $^{23}$Na FT NMR spectra with $H_0$ (=5.8701 T) applied along the direction of the magic angle in the $ab$ plane where the electric quadrupole splitting vanishes as shown in the inset of Fig. 1. The $T$ dependence of $^{23}K$ obeys above 180 K the Curie-Weiss law $^{23}K=C/(T-\Theta)$ with $C=0.17$ K and the Weiss temperature $\Theta=96$ K. It should be noted that the positive value of $\Theta$ indicates the presence of the FM correlation. The similar behavior was also observed in the $T$ dependence of the $^{51}$V Knight shift. The origin of the FM correlation is closely related to the multi-orbital state at the Fermi level in NaV$_2$O$_4$. The mirror symmetry at the V sites leads to the splitting of the $t_{2g}$ orbital into the doublet, $d_{yz}$ and $d_{zx}$, and the singlet $d_{xy}$. The doublet orbital spreads to the rung direction in the double chain, whereas the singlet spreads to the leg direction. Then 3$d$ electrons which occupy the doublet are considered to generate the FM interaction due to the Hund coupling, which is the origin of the FM correlation observed in the paramagnetic state, whereas 3$d$ electrons on the $d_{xy}$ orbital lead to the AFM interaction. Thus the competition between the FM and AFM interactions is expected in the double chain.

In a magnetically ordered state, spontaneous magnetic moments generally generate an internal field $H_n$ at a nuclear site. Then the NMR frequency $\nu_{\text{res}}$ is written as

$$\nu_{\text{res}} = 2\pi \gamma_n |H_0 + H_n|,$$

where $\gamma_n$ is the nuclear gyromagnetic ratio. The inset in Fig. 2 (a) shows $^{23}$Na NMR spectrum with $H_0$ (=5.8701 T) $\parallel b$ at several temperatures. One central and two satellite lines split by the electric quadrupole interaction are observed above $T_N$, whereas the characteristic spectra with six peaks appear below $T_N$. The spectrum below $T_N$ is composed of three broad spectra due to one central and two satellite transitions. Each broad spectrum has two peaks denoted by the
arrows in Fig. 2 (a) and clearly shows a broad distribution of $H_0$ at the Na site. The difference between the NMR frequencies denoted by the red arrows in the spectrum of the central transition $\Delta \nu_{\text{res}}$ shows the $T$ dependence, as presented in Fig. 2 (a), which obeys the $T$ dependence of the ordered magnetic moment.

Figure 2. (Color online) (a) Temperature dependence of the difference between resonance frequencies of the peak positions denoted by the red arrows in the $^{23}$Na central spectra, $\Delta \nu_{\text{res}}$, with $H_0$ (=5.8701 T) applied along the $b$ axis in NaV$_2$O$_4$. The inset shows the temperature dependence of the $^{23}$Na NMR spectrum with $H_0 \parallel b$. (b) The angular dependence of $\Delta \nu_{\text{res}}$ with $H_0$ (=3.0 T) rotated in the $ab$ and $bc$ planes at 20 K in NaV$_2$O$_4$.

Figure 3. $^{51}$V NMR spectrum under zero external field at 4.2K in NaV$_2$O$_4$. 
At $H_0$=3.0 T and $T$=20 K in the AFM3 phase of NaV$_2$O$_4$, the $^{23}$Na NMR spectra similar to the inset of Fig. 2 (a) were observed with $H_0$ applied along any direction. Figure 2 (b) shows the angular dependence of $\Delta \nu_{\text{res}}$ with $H_0$ rotated in the $ab$ and $bc$ planes. This angular dependence is governed by the spin structure via the classical dipole interaction from the magnetic moments at the V sites. The fact that $\Delta \nu_{\text{res}}$ for $H_0 \perp a$ is larger than that for $H_0 \parallel a$ indicates that the direction of the magnetic moments may be parallel to the $bc$ plane, if an inter-chain ferromagnetic spin configuration is assumed. The broad spectra observed in the present NMR experiments clearly reject the collinear AF spin structures proposed in the magnetic susceptibility [2] and $\mu$SR measurements [4]. Thus we discuss in the following two models which can reproduce the broad $^{23}$Na NMR spectra and the angular dependence of $\Delta \nu_{\text{res}}$. One is an incommensurate helical structure and the other is an incommensurate spin density wave (SDW) structure proposed by the neutron scattering measurement [5]. However, the SDW model cannot explain the $^{51}$V NMR spectrum under zero external field at 4.2 K as shown in Fig. 3, because a spectrum spread down to zero frequency expected for the SDW model is inconsistent with the spectrum observed in the frequency range 85-140 MHz. This $^{51}$V spectrum indicates an incommensurate spin structure in the AFM3 phase and supports the helical model. Thus we propose the incommensurate helical spin structure which is reasonably expected to appear by the competition between the FM and AFM interactions in the double chain.

4. Conclusion
We have performed $^{23}$Na and $^{51}$V NMR measurements to investigate the frustration effect on the local magnetic properties of NaV$_2$O$_4$. We confirmed that the ferromagnetic correlation exists in the paramagnetic state from the temperature dependence of the $^{23}$Na Knight shift. We also discussed the origin of the ferromagnetic interaction on the basis of the 3$d$ orbital shift. In the magnetically ordered state, we proposed the incommensurate helical spin structure which appears due to the competition between the ferromagnetic and antiferromagnetic interactions in the double chain.

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