Local Magnetic Properties of Na$_{1-x}$Ca$_x$V$_2$O$_4$ with Double Chains Investiagted by $^{51}$V NMR

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Abstract. We have performed $^{51}$V NMR measurements to investigate local magnetic properties of Na$_{1-x}$Ca$_x$V$_2$O$_4$ with the CaFe$_2$O$_4$ type structure composed of double chains. The $^{51}$V Knight shift due to the spin susceptibility in an itinerant antiferromagnet NaV$_2$O$_4$ is found to obey the Curie-Weiss law with the positive Weiss temperature, indicating the ferromagnetic correlation in the paramagnetic state. The NMR spectrum at 4.2 K may be reproduced by an incommensurate spin structure in the antiferromagnetic state of NaV$_2$O$_4$. Also the NMR results at 4.2 K on Na$_{1-x}$Ca$_x$V$_2$O$_4$ are consistent with the phase diagram proposed from the $\mu^+\mu$SR measurements, namely, antiferromagnetic, spin-glass-like and mixture phases.

1. Introduction
The metal-insulator transition (MIT) is one of the most interesting phenomena in strongly correlated electron systems [1]. The MIT in mixed-valence vanadium oxides with a quasi-one-dimensional structure such as $\beta$-Na$_{0.33}$V$_2$O$_5$ [2, 3] and K$_2$V$_8$O$_{16}$ [4, 5] have been intensively investigated from the aspects of the MIT accompanied by the charge ordering. Recently Na$_{1-x}$Ca$_x$V$_2$O$_4$ with the CaFe$_2$O$_4$ type structure similar to the crystal structure of K$_2$V$_8$O$_{16}$ were reported to be a candidate of the vanadium oxides with the carrier-controlled MIT [6, 7].

Na$_{1-x}$Ca$_x$V$_2$O$_4$ has a V$_8$O$_{16}$ framework composed of double chains of edge sharing V(1)O$_6$ or V(2)O$_6$ octahedra as seen in Fig. 1 where the crystal structure of NaV$_2$O$_4$ is presented [6]. Na or Ca atoms are located in a tunnel of the framework. The double chain structure is expected to have a low dimensional electronic structure with the geometrical frustration. The formal valence of the vanadium ion changes from +3.5 to +3 with increasing $x$ from 0 to 1 in Na$_{1-x}$Ca$_x$V$_2$O$_4$, resulting in physical properties strongly dependent on $x$. The samples with $x \leq 0.23$ are metallic and show three antiferromagnetic (AF) orders AF1-AF3, that are dependent on $x$, external magnetic field and temperature, with the Néel temperature $T_N$ from 140 K to 100 K depending on $x$ [7]. The samples with $0.23 \leq x \leq 0.58$ undergo the MIT, whereas they are insulating for $x \geq 0.58$. Recently, the magnetic phase diagram and the spin structures in the AF phases were proposed from the $\mu^+\mu$SR study [8]. However, the local magnetic properties of Na$_{1-x}$Ca$_x$V$_2$O$_4$ have not been well clarified.

In this study, we have made $^{51}$V NMR measurements to investigate the local magnetic properties of Na$_{1-x}$Ca$_x$V$_2$O$_4$. We found that there is a ferromagnetic correlation in the paramagnetic phase of NaV$_2$O$_4$. Incommensurate AF orders may appear in the AF phases.
of Na$_{1-x}$Ca$_x$V$_2$O$_4$ with $x<0.23$. We also report that the NMR results at 4.2 K are consistent with the phase diagram proposed from the $\mu^+\text{SR}$ measurements.

2. Experiments

Polycrystalline samples of Na$_{1-x}$Ca$_x$V$_2$O$_4$ with $x=0, 0.17, 0.23, 0.33, 0.5, 0.67, 0.92$, and 1 were prepared by a solid-state reaction method under a pressure of 6 GPa, using CaV$_2$O$_4$, Na$_4$V$_2$O$_7$ and V$_2$O$_3$ powders as starting materials [7]. $^{51}$V Fourier-transformed (FT) NMR spectra were measured in a magnetic field of $H_0=5.8701$ T by using a pulsed spectrometer. The $^{51}$V Knight shift was determined as $K=\left(\nu_{\text{res}}-\nu_0\right)/\nu_0$ where $\nu_{\text{res}}$ and $\nu_0$ (=65.704 MHz) are resonance frequencies in the samples and 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 2 (a) shows $^{51}$V FT NMR spectra at various temperatures above $T_N=140$ K in the itinerant AF magnet NaV$_2$O$_4$. The characteristic spectra, which come from the V(1) and V(2) sites, with four peaks denoted by the symbols A-D in Fig. 2 (a) cannot be explained by a randomly oriented power pattern with an anisotropic Knight shift. NMR experiments on a single crystal are desired to understand the NMR spectra and the site assignment. However, the temperature $T$ dependence of the $^{51}$V Knight shifts $^{51}K$, which was to found to follow magnetic susceptibility $\chi$, determined from the A-D peaks is useful for clarifying the magnetic interaction as discussed below.

The Knight shift $^{51}K$ can be generally decomposed into spin and orbital parts as $^{51}K=^{51}K_{\text{spin}}+^{51}K_{\text{orb}}$. The orbital part $^{51}K_{\text{orb}}$ is expressed as

$$^{51}K_{\text{orb}} = \frac{A_{\text{orb}}}{N_A \mu_B} \chi_{\text{orb}},$$

where $N_A$ is the Avogadro’s number, $\mu_B$ is the Bohr magneton and $\chi_{\text{orb}}$ is the orbital susceptibility. Also $A_{\text{orb}}$ is the orbital hyperfine coupling constant written by $A_{\text{orb}}=2\mu_B k \langle r^{-3} \rangle$ where $k$ is a reduction factor in a metal and $\langle r^{-3} \rangle$ is an expectation value of $r^{-3}$ for a 3d wave function [9]. From the conventional $^{51}K$ versus $\chi$ plots, we obtain the values of $^{51}K_{\text{orb}}$ as 0.46-1.2 %, assuming $A_{\text{orb}}=346$ kOe/$\mu_B$ evaluated from $k=0.8$ and $\langle r^{-3} \rangle=3.451$ a.u., the average value of $\langle r^{-3} \rangle=3.217$ a.u. for V$^{3+}$ and $\langle r^{-3} \rangle=3.684$ a.u. for V$^{4+}$ [9]. After subtracting $^{51}K_{\text{orb}}$ from $^{51}K$, we obtain the $T$ dependence of $1/^{51}K_{\text{spin}}$ for the A-D peaks as shown in Fig. 2 (b). The shifts $^{51}K_{\text{spin}}$ obey the Curie-Weiss law $^{51}K_{\text{spin}}=C/(T-\Theta)$ with $C=6.8-12$ K and the Weiss temperature $\Theta=84-87$ K for the A-D peaks as seen in Fig. 2 (b). It should be noted that the positive values of $\Theta$ indicate the development of the ferromagnetic correlation, which may come
from the ferromagnetic interaction in the double chain as discussed in $\text{K}_2\text{V}_8\text{O}_{16}$ [10] with the structure similar to $\text{NaV}_2\text{O}_4$, in the paramagnetic state of $\text{NaV}_2\text{O}_4$.

**Figure 2.** (a) Temperature dependence of the $^{51}\text{V}$ NMR spectrum at 5.8701 T in the powder sample of $\text{NaV}_2\text{O}_4$. (b) Temperature dependence of the $^{51}\text{V}$ Knight shift due to the spin susceptibility $^{51}\text{K}_{\text{spin}}$ in $\text{NaV}_2\text{O}_4$. The solid lines represent the fitted results of the data to the relation $1/^{51}\text{K}_{\text{spin}} = (T - \Theta)/C$ where $C$ is a constant and $\Theta$ is the Weiss temperature.

**Figure 3.** $^{51}\text{V}$ NMR spectra under zero external field at 4.2 K in $\text{Na}_{1-x}\text{Ca}_x\text{V}_2\text{O}_4$.

The $^{51}\text{V}$ NMR spectrum in $H_0$ was wiped out below $T_N=140$ K due to the AF order in $\text{NaV}_2\text{O}_4$, whereas we observed the $^{23}\text{Na}$ NMR spectrum with a characteristic line width.
which shows the $T$ dependence following the AF order parameter (not shown). In magnetically ordered states, spontaneous magnetic moments allow us to observe NMR spectra, that provide information on the spin structure, even in zero external field. Figure 3 shows frequency-swept $^{51}$V NMR spectra at 4.2 K under zero external field in NaV$_2$O$_4$ and Na$_{1-x}$Ca$_x$V$_2$O$_4$. In NaV$_2$O$_4$, the broad spectrum observed in the frequency range 85-140MHz with two peaks at 125 and 134 MHz indicates not the collinear AF spin structure proposed from the $\mu^+\text{SR}$ experiment [8] but an incommensurate structure in the AF3 phase of NaV$_2$O$_4$. Also in the AF1 phase of the $x=0.17$ sample, we observed a broad spectrum with a peak at 167 MHz and a step at 120 MHz that is explained not by the collinear model proposed in the $\mu^+\text{SR}$ study [8] but by another incommensurate order. In the $x$ range of $0.23<x\leq0.5$, we observed no intrinsic spectrum except a spectrum at $\sim208$ MHz which comes from an impurity of V$_2$O$_3$ [11]. This may occur due to randomness of the internal field in a spin-glass-like state proposed from the $\mu^+\text{SR}$ results. The end member CaV$_2$O$_4$, an insulating antiferromagnet with $T_N=78$ K, has a spectrum above $\sim200$ MHz that is consistent with the reported NMR spectrum [12]. Observation of the NMR spectra for $0.5<x<1$ similar to the spectrum of $x=1$ shows that the NMR spectra are ascribed to CaV$_2$O$_4$. Thus the present results for $x>0.5$ are concluded to have a mixture phase composed of CaV$_2$O$_4$ and the spin-glass-like sample. The present NMR results with varying $x$ at 4.2 K in Na$_{1-x}$Ca$_x$V$_2$O$_4$ are consistent with the phase diagram proposed from the $\mu^+\text{SR}$ study [8], where the antiferromagnetic ($0\leq x \leq0.23$), spin-glass-like ($0.23\leq x \leq0.5$) and mixture ($0.5<x<1$) phases appear.

4. Conclusion
We have performed $^{51}$V NMR measurements to investigate local magnetic properties of Na$_{1-x}$Ca$_x$V$_2$O$_4$ with double chains. We found that the ferromagnetic correlation exists in the paramagnetic state of the itinerant antiferromagnet NaV$_2$O$_4$. It is also concluded that the NMR spectra for $x\leq0.23$ at 4.2 K may be explained by incommensurate antiferromagnetic spin structures. The NMR results at 4.2 K for Na$_{1-x}$Ca$_x$V$_2$O$_4$ were consistent with the phase diagram proposed by the $\mu^+\text{SR}$ measurements.

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