NMR study of magnetic excitation in LiVX₂ (X = O, S)

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Abstract. Magnetic excitation in the two-dimensional triangular lattice LiVO₂ and its itinerant analogue LiVS₂ are investigated by ⁵¹V- and ⁷Li-NMR experiments. The nuclear spin-lattice relaxation rate ¹/T₁ on ⁵¹V and ⁷Li nuclei shows thermally activated behavior with different size of spin gap, Δ/k_B ∼ 3400 K for LiVO₂ and ∼ 1900 K for LiVS₂, below the transition temperature T_c from magnetic to non-magnetic ground state. In ⁵¹(¹/T₁(T))/⁵¹(¹/T₁(T_c)) vs. T/T_c plot, the normalized relaxation rate for both materials seems to fall on the same curve. This scaling behavior indicates that the ground states of LiVO₂ and LiVS₂ are the same, i.e., V³⁺ (3d², S = 1) spins form spin singlet with the formation of triangular vanadium clusters, although the replacement of oxygen by sulfur may broaden the band width and largely suppresses T_c from ∼ 500 K in LiVO₂ to ∼ 310 K in LiVS₂. However, the magnetic properties in the high temperature phase are different between LiVO₂ and LiVS₂. The value of ⁷(¹/T₁(T)) in LiVS₂ becomes smaller with decreasing temperature, which suggests the development of pseudogap above T_c, in qualitatively consistent with the results from the magnetic susceptibility and the small change in entropy at T_c. This is a contrast to the case in LiVO₂ where ⁵¹(¹/T₁(T)) is proportional to ¹/T and it is explained by a localized spin model well above T_c.

1. Introduction

Two-dimensional triangular lattice has attracted much attention concerning the unusual frustration effects and the exotic character of the ground state. LiVO₂ is regarded as one of the ideal model compounds of such a system and, therefore, many experimental and theoretical works have been devoted to this material for several decades [1, 2, 3, 4, 5, 6]. LiVO₂, in which the magnetic V³⁺ ions (3d², S = 1) form a two-dimensional triangular lattice, is a paramagnetic insulator with strong antiferromagnetic interaction among well localized 3d electron spins at high temperature. Upon cooling, at T_c ∼ 500 K, LiVO₂ exhibits a first order phase transition to a spin singlet state accompanied by the formation of triangular vanadium clusters (trimers). This exotic magnetic ground state have been discussed in terms of novel interplay between spin and orbital degrees of freedom in the two-dimensional triangular lattice [7].

Recently, its itinerant analogues LiVS₂ and LiVSe₂ have been synthesized and systematically investigated by Katayama et al. [8]. The replacement of oxygen by larger anions such as S and
Se is considered to increase the overlap between 3d of V and p electrons of O and S (Se) and, as a result, broaden the band width. Actually, \( T_c \approx 310 \text{ K} \) in LiVS \(_2\) is markedly suppressed by the replacement from \( T_c \approx 500 \text{ K} \) in LiVO \(_2\). The ground state is, however, robust, i.e., V\(^{3+}\) spins in LiVS \(_2\) form a spin singlet with the formation of vanadium trimer below \( T_c \) as realized in LiVO \(_2\). The formation of vanadium trimer is evidenced by the electron diffraction and the EXFS measurements. More itinerant analogue LiVSe \(_2\) is a paramagnetic metal down to 2 K, i.e., the spin singlet state disappears. The schematic phase diagram in LiVX \(_2\) (X = O, S and Se) system is represented in Fig. 1 from Ref.[8]. The phase diagram indicates that LiVS \(_2\) is located near the border between paramagnetic metal and spin singlet insulating phases.

Interestingly, in the high temperature phase of LiVS \(_2\), the magnetic susceptibility \( \chi \) exhibits strong temperature dependence, which is similar to the pseudogap behavior found in underdoped superconducting cuprates [9]. The fact that the change in entropy of LiVS \(_2\) at \( T_c \) is about one-half as small as that of LiVO \(_2\) also supports the existence of pseudogap. To investigate these exotic magnetic properties in LiVO \(_2\) and LiVS \(_2\) from a microscopic view point, we have measured nuclear spin-lattice relaxation rate \( \frac{1}{T_1} \) by \(^{51}\text{V-NMR}\) and \( \frac{1}{T_1} \) by \(^{7}\text{Li-NMR}\) experiments. Here, we stress that NMR may be one of the most powerful tools to investigate a spin singlet and a pseudogap, because \( 1/T_1 \) probes low energy magnetic excitation and the pseudogap in underdoped superconducting cuprates was found by NMR for the first time [9].

2. Experimental

The detailed preparation method of the powder samples of LiVO \(_2\) and LiVS \(_2\) has been already reported elsewhere [8]. The synthesized samples were characterized crystallographically with X-ray diffractometer, and magnetically with SQUID magnetometer. The temperature dependence of \( \chi \) indicates that the transition from the non-magnetic ground state to the magnetic one is of a first order and occurs at \( T_c \approx 310 \text{ K} \) for LiVS \(_2\) and at \( T_c \approx 500 \text{ K} \) for LiVO \(_2\) in heating process. The obtained data were in accordance with those reported previously [6, 8, 10].

For the present NMR measurements, the powder samples were enclosed in a quartz tube with He gas as a heat exchanger to avoid possible degeneration of the samples in atmosphere. The \(^{51}\text{V-}\) and \(^{7}\text{Li-NMR}\) signals were observed by the spin-echo technique and nuclear spin-lattice relaxation rates \( \frac{1}{T_1} \) were measured by the saturation recovery method. A longitudinal recovery of nuclear magnetization \( m(t) \), \( t \text{ sec} \) after a saturating pulse, is theoretically
expressed by
\[ \frac{m(\infty) - m(t)}{m(\infty)} = 0.0119 \exp\left(\frac{-t}{T_1}\right) + 0.0682 \exp\left(\frac{-6t}{T_1}\right) + 0.206 \exp\left(\frac{-15t}{T_1}\right) + 0.714 \exp\left(\frac{-28t}{T_1}\right) \]
for the transition between \( I_z = -1/2 \leftrightarrow +1/2 \) of the nuclear spin \( I = 7/2 \) [11]. This is the case for our measurements of \( ^{51}(1/T_1) \) by \(^{51}\)V-NMR . \(^{51}(1/T_1) \) is determined by the fits of the theoretical curve to the measured \( m(t) \) at each temperature. The high quality of the fits guarantees validity of the measurements [12]. In the measurements of \(^7(1/T_1) \) by \(^7\)Li-NMR, the measured \( m(t) \) follows \( (m(\infty) - m(t))/m(\infty) = \exp(-t/T_1) \). Such a single exponential relaxation is expected if all the satellite lines overlap the central line in NMR spectrum [11]. This overlap is, generally, likely to occur in \(^7\)Li-NMR experiments, partly because the nuclear quadrupole moment of \(^7\)Li nuclei \( ^7Q \) is small as \( ^7Q = -4 \times 10^{-26} \text{ cm}^2 \). Actually, \(^7\)Li-NMR spectrum in LiVO\(_2\) and LiVS\(_2\) consists of single line at all the measured temperature [13].

3. Results and Discussion

3.1. \(^{51}\)V-NMR

Figure 2 shows the temperature dependence of nuclear spin-lattice relaxation rate \(^{51}(1/T_1) \) for LiVO\(_2\) and LiVS\(_2\) by open and filled circles, respectively. The overall temperature dependence of \(^{51}(1/T_1) \) in LiVX\(_2\) (X = O, S) is quite similar each other and show thermally activated behavior below \( T_c \) except the data at low temperature. We show the Arrhenius plot of the data in the bottom right and the upper left of the figure for LiVO\(_2\) and LiVS\(_2\), respectively. The linear relation between \( \log^{51}(1/T_1) \) and \( 1/T \) clearly confirms the thermally activated behavior. These results indicate that the electronic density of states or magnetic spin excitation has an energy gap at the Fermi surface in consistent with the formation of spin singlet in V\(^{3+}\) ions. The formation of spin singlet is also indicated by non-magnetic natures inferred from temperature independent Knight shift below \( T_c \) (not shown) in agreement with the previous reports [2, 4, 13].

The activation-type relaxation rate varies following
\[ \frac{1}{T_1} \propto \exp\left(\frac{-\Delta}{k_BT}\right), \]

Figure 2. Temperature dependence of \(^{51}(1/T_1) \) in LiVO\(_2\) (open circles) and LiVS\(_2\) (filled circles) measured by \(^{51}\)V-NMR. Insets: Arrhenius plot of \(^{51}(1/T_1) \) for LiVO\(_2\) (bottom right) and \(^{51}(1/T_1) \) of LiVS\(_2\) (upper left). The solid lines represent the fits by the activation-type curves to the data.
where Δ/k_B is the size of energy gap in the unit of Kelvin and k_B is the Boltzmann constant. The best fit to the data is represented by solid lines in the main panel of Fig. 2 and its insets. In the fits, we adopt the data in the temperature range 180 K < T < T_c for LiVO_2 and 150 K < T < T_c for LiVS_2. The size of energy gap Δ/k_B is estimated to be about 3400 K for LiVO_2 and 1900 K for LiVS_2 from the fits.

At low temperature, 51(1/T_1) becomes weakly temperature dependent and deviates from the thermally activated behavior below 180 K for LiVO_2 and 150 K for LiVS_2. The deviation is most probably due to possible fluctuations of paramagnetic impurity spins and, therefore, extrinsic, because a relaxation rate is generally expected to be independent of temperature if independent fluctuations of local magnetic moments dominate a relaxation process of nuclear spin [14, 15]. Actually, there exist paramagnetic impurity spins and an amount of them is estimated to be as small as ~ 1 % from a Curie tail in χ at low temperature [8]. The weakly temperature dependent values of 51(1/T_1) ~ 0.1 s⁻¹ in LiVO_2 is the same order of magnitude as that in LiVS_2. This result suggests that hyperfine coupling constants on 51V nuclei in LiVO_2 and LiVS_2 are comparable, if we assume that spin-fluctuation properties of paramagnetic impurity are similar for both materials.

The estimated sizes of the spin gap are in good agreement with those from 7(1/T_1) by 7Li-NMR as discussed later for both materials, but the size of it for LiVO_2 is larger than ~ 1600 K reported in the literature [3]. The difference may originate from the different temperature range adopted for the fits, where the wider temperature range gives the smaller size of the spin gap due to the weakly temperature dependent region at low temperature. Although the estimation of the spin-gap size somewhat depends on fits, one could compare the temperature dependence of 51(1/T_1) in LiVO_2 and LiVS_2 as follows. Fig. 3 shows 51(1/T_1(T)) normalized by the value at T_c against T/T_c for LiVO_2 (open circles) and LiVS_2 (filled circles). In this plot, the normalized relaxation rate for both materials seems to fall on the same curve below T_c except at low temperature. This scaling behavior indicates that the difference in T_c of LiVO_2 and LiVS_2 is closely associated with the difference in the size of spin gap and that the ground state of them are essentially same. In other words, although the itinerancy of 3d electrons in LiVS_2 are increased from that in LiVO_2, V^{3+} spins in LiVS_2 form the spin singlet with the formation of vanadium trimer in the ground state as realized in LiVO_2 in the ground state.
The intensity of the $^{51}$V-NMR signal decreases rapidly on approaching $T_c$ and the signal was not measurable above $T_c$ in our experimental condition for both materials. The rapid decrease in the signal is most probably due to the decrease in spin-spin relaxation time $T_2$ near the transition temperature, i.e., a critical slowing down [13]. Nonetheless, one could estimate the value of $^{51}(1/T_1(T))$ divided by temperature at $T_c$, $^{51}(1/T_1(T_c)T_c)$ to be 4.8 s$^{-1}$K$^{-1}$ and 0.44 s$^{-1}$K$^{-1}$ for LiVO$_2$ and LiVS$_2$, respectively, from the extrapolation of the data below $T_c$. $^{51}(1/T_1(T_c)T_c)$ in LiVS$_2$ is one order of magnitude smaller than that in LiVO$_2$, although the hyperfine coupling constants are comparable for both materials. This result suggests that the magnetic property is different between LiVS$_2$ and LiVO$_2$ in the high temperature phase. The existence of pseudogap above $T_c$, suggested from the temperature dependence of $\chi$ and the small change in the entropy at $T_c$ [8], may explain the much smaller value of $^{51}(1/T_1(T_c)T_c)$ in LiVS$_2$.

3.2. $^7$Li-NMR
The intensity of $^7$Li-NMR signal is larger than that of $^{51}$V-NMR one. This is partly because two satellite lines overlap the central line in the $^7$Li-NMR spectrum and spin-spin relaxation in $^7$Li nuclei is much slower than that in $^{51}$V one. The larger signal intensity enables us to measure the nuclear spin-lattice relaxation rate $^7(1/T_1(T))$ up to the higher temperature, $\sim$ 500 K. In Fig. 4, we show the temperature dependence of $^7(1/T_1)$ in LiVO$_2$ and LiVS$_2$ by open and filled circles, respectively. In a limited temperature range, 320 K $< T < T_c$ for LiVO$_2$ and 260 K $< T < T_c$ for LiVS$_2$, we find the thermally activated behavior characterized by Eq. (1). The best fits to the data, represented by solid lines in Fig. 4, yield the size of spin gap $\Delta/k_B$ $\sim$ 3100 K for LiVO$_2$ and $\sim$ 2000 K for LiVS$_2$. These values are in good agreement with those obtained by the $^{51}$V-NMR measurements and, therefore, support the discussion in the previous subsection. At low temperature, $^7(1/T_1)$ shows weak temperature dependence and deviates from the thermally activated behavior for both materials. The deviation may be extrinsic, because it most probably originates from the independent fluctuations of paramagnetic impurity spins as discussed in the previous subsection.

To focus on the high temperature phase of LiVS$_2$, we show the temperature dependence of $^7(1/T_1T)$ above 200 K in the inset of Fig. 4. The value of $^7(1/T_1T)$ in LiVS$_2$ becomes smaller with decreasing temperature in the high temperature phase above $T_c$. This result is a contrast to...
the case in LiVO$_2$ where $^{51}(1/T_1T)$ is proportional to $1/T$ well above $T_c$ and it is explained by the localized spin model with $S = 1$ [2]. The decrease in $^7(1/T_1T)$ of LiVS$_2$ indicates the existence of gap in magnetic excitation or Li$^+$ diffusion. The latter is, however, ruled out, because no motional narrowing is observed in the $^7$Li-NMR spectrum up to 500 K, i.e., the line width of $^7$Li-NMR spectrum, $\sim 22$ Gauss, is independent of temperature in the measured temperature range. The temperature dependence of $^7(1/T_1T)$, therefore, suggests the opening of pseudogap in the high temperature phase, where the short-range ordering of the spin singlet may develop.

4. Conclusions

We have measured the nuclear spin-lattice relaxation rate $1/T_1$ on $^{51}$V and $^7$Li nuclei in the two-dimensional triangular lattice LiVO$_2$ and its itinerant analogue LiVS$_2$. In the low temperature phase below $T_c$, the temperature dependence of $1/T_1$ on both $^{51}$V and $^7$Li nuclei consistently follows the thermally activated behavior, $1/T_1 \propto \exp(-\Delta/k_BT)$, and evaluates the magnitudes of spin gap: $\Delta/k_B \sim 3400$ K for LiVO$_2$ and $\sim 1900$ K for LiVS$_2$. In $^{51}(1/T_1(T))/^{51}(1/T_1(T_c))$ vs. $T/T_c$ plot, the normalized relaxation rate for both materials seems to fall on the same curve. These results indicate that the ground state of LiVS$_2$ is essentially the same as that in LiVO$_2$, where V$^{3+}$ ($3d^2, S = 1$) spins form the spin singlet with the formation of vanadium trimer, although the replacement of oxygen by sulfur broadens the band width and markedly suppresses $T_c$ from $\sim 500$ K in LiVO$_2$ to $\sim 310$ K in LiVS$_2$. In the high temperature phase of LiVS$_2$ above $T_c$, the nuclear spin-lattice relaxation rate divided by temperature $^7(1/T_1T)$ decreases on cooling in LiVS$_2$, exhibiting a pseudogap-like behavior. This is a contrast to the case in LiVO$_2$ where $^{51}(1/T_1T)$ is proportional to $1/T$ well above $T_c$ and it is explained by a localized spin model.

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