Metal-insulator transition in the Hollandite vanadate $\text{K}_2\text{V}_8\text{O}_{16}$ investigated by $^{51}\text{V}$ NMR measurements

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Abstract. $^{51}\text{V}$ NMR measurements have been made on powdered samples to investigate the metal-insulator (MI) transition and the local magnetic properties of the Hollandite vanadate $\text{K}_2\text{V}_8\text{O}_{16}$ which undergoes the MI transition at $T_{\text{MI}} \sim 170$ K. An asymmetric $^{51}\text{V}$ NMR spectrum in the metallic phase has the $T$-dependent negative Knight shift $K$. The two NMR spectra appears around $T_{\text{MI}}$, showing the coexistence of the metallic and insulating phases in consistent with the two-step first-order transition. The temperature dependence of $K$ and the $^{51}\text{V}$ nuclear spin-lattice relaxation rate indicates the presence of the ferromagnetic spin fluctuations in the metallic phase. A $^{51}\text{V}$ NMR spectrum observed below $T_{\text{MI}}$ has the temperature-independent $K \sim 0.35\%$, showing the presence of the nonmagnetic ground state.

1. Introduction

Metallic and insulating phases near the metal-insulator (MI) transition in $3d$ transition metal oxides with strongly correlated electron systems give rise to the fascinating phenomena such as high-temperature superconductivity, colossal magnetoresistance, and so on [1]. In particular, mixed-valence vanadium oxides with a quasi-one-dimensional (quasi-1D) structure $\beta\text{-A}_{0.33}\text{V}_2\text{O}_3$ ($\text{A} = \text{Na}, \text{Li}, \cdots$) have attracted interests from the aspects of the MI transition accompanied by the charge ordering (CO) and superconductivity under high pressure [2, 3, 4, 5, 6, 7]. As other candidate of the quasi-1D conductors, the vanadium oxides with the Hollandite-type structure, $\text{A}_x\text{V}_8\text{O}_{16}$ ($\text{A} = \text{K}, \text{Bi}, \cdots$ with $x \leq 2$), have been investigated to look for unconventional phenomena near the MI transition [8, 9, 10, 11]. The Hollandite vanadates have a tubular $\text{V}_8\text{O}_{16}$ network and $\text{A}$ cations in the tunnels of the $\text{V}_8\text{O}_{16}$ framework as presented in Fig. 1. The $\text{V}_8\text{O}_{16}$ framework is composed of double chains which are formed by the edge-shared VO$_6$ octahedra. Recently, Isobe et al. synthesized a Hollandite vanadate $\text{K}_2\text{V}_8\text{O}_{16}$ by a solid state reaction method under high pressure, and investigated structural and electromagnetic properties [11]. They found the MI transition with a two step jump in the resistivity versus temperature curve at $T_{\text{MI}} \sim 170$ K. The MI transition is accompanied by a structural transition from the tetragonal to monoclinic structures. In the low temperature insulating phase, the superlattice of $\sqrt{2}a \times \sqrt{2}a \times 2c$ was observed in the x-ray diffraction on a single crystal of $\text{K}_2\text{V}_8\text{O}_{16}$. They proposed a CO model of $V^{4+}$-$\cdot$-$V^{4+}$ and $V^{3+}$-$\cdot$-$V^{3+}$ pairs with two double chains formed by $V^{4+}$

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and V$^{3+}$ and one double chain by V$^{4+}$. Horiuchi et al. discussed the CO patterns from the calculation of the Madelung energy and furthermore the orbital-ordering pattern based on the exact-diagonarization method on small clusters [12]. However, the CO pattern and the local magnetic properties closely related to the MI transition have not been clarified.

In this study, we have made $^{51}$V NMR measurements on powder samples to study the MI transition and the local magnetic properties of the Hollandite vanadate K$_2$V$_8$O$_{16}$. The temperature $T$ dependence of the $^{51}$V Knight shift $K$ and the nuclear spin-lattice relaxation rate $1/T_1$ are presented. These experimental results indicate the presence of the ferromagnetic spin fluctuations in the metallic and the nonmagnetic ground state in the insulating phase.

2. Experimental procedure

Powder samples of K$_2$V$_8$O$_{16}$ were prepared by a solid state reaction method under high pressure [11]. The samples were confirmed to be almost of a single phase of K$_2$V$_8$O$_{16}$ with a slight impurity by powder x-ray diffraction. Magnetic susceptibility was measured using a SQUID magnetometer. Field-swept $^{51}$V NMR spectra were taken by sweeping an external field of a superconducting magnet with a boxcar integrator at 90.0 MHz. The $^{51}$V nuclear spin-lattice relaxation rate was measured for the NMR spectrum maximum by the inversion recovery method.

3. Experimental results and discussion

Figure 2 shows the $T$ dependence of the field-swept $^{51}$V NMR spectrum taken at 90.0 MHz with increasing $T$ in K$_2$V$_8$O$_{16}$. In the $T$ range 145 K<$T<$300 K, we observed an asymmetric $^{51}$V NMR spectrum coming from the metallic phase with the $T$-dependent negative Knight shift and a weak spectrum with the $T$-independent $K$~0.24 % from an impurity. On the other hand, a symmetric spectrum form the insulating phase appears with almost $T$-independent $K$~0.35 % below ~180 K. The increase of the spectrum width with decreasing $T$ is due to the increase of magnetic susceptibility as mentioned below. In the $T$ range 145 K<$T<$180 K around $T_{MI}$, it should be noted that both spectra from the metallic and insulating phases coexist as seen in Fig. 1. This coexistence is consistent with the two-step first-order MI transition where the magnetic susceptibility and the electric resistivity are reported to show significant hysteresis [11].

The $T$ dependence of magnetic susceptibility is presented in Fig. 3 (a). The magnetic susceptibility shows a gradual reduction in the $T$ range 145 K<$T<$180 K and the upturn following the Curie law at low temperatures which is ascribed to a magnetic impurity [11]. The Knight shift $K$ is proportional to the local magnetic susceptibility. We determine $K$ from the field of the NMR spectrum peak in Fig. 2, because the asymmetric spectra in the metallic phase cannot be explained by a powder pattern with an anitoropic Knight shift. In order to clarify the anisotropic shift, NMR experiments on a single crystal are desired. Figure 3 (b) shows the
Figure 2. Field-swept $^{51}$V NMR spectra taken at various temperatures and 90.0 MHz in $K_2V_8O_{16}$.

Figure 3. Temperature dependence of (a) magnetic susceptibility and (b) the $^{51}$V Knight shift in $K_2V_8O_{16}$. The solid curve represents the fitted result of the $K$ data to the Curie Weiss law with a constant term.

$T$ dependence of $K$ which has the Curie Weiss (CW) term with the Weiss temperature of 112 K in the $T$ range 145 K<$T<$300 K. One notes that $K$ does not follow bulk magnetic susceptibility particularly in the range of 145 K<$T<$180 K. In this range there exit V sites in both metallic and insulating phases as mentioned above, and the fraction of the metallic phase decreases with decreasing $T$. This is the reason why magnetic susceptibility gradually reduces near $T_{MI}$. In the insulating phase, the NMR spectrum with the almost $T$-independent Knight shift $K\sim 0.35\%$, the orbital Knight shift in the insulating phase, clearly shows the presence of nonmagnetic vanadium sites. Isobe et al. proposed the model of the CO pattern composed of $V^{4+}$-$V^{4+}$ and $V^{3+}$-$V^{3+}$ pairs which form spin singlet states, resulting in the nonmagnetic ground state [11]. This model is consistent with the observation of the nonmagnetic NMR spectrum observed below $T_{MI}$, although the CO pattern cannot be determined in the present NMR study.

The nuclear spin-lattice relaxation rate $1/T_1$ is well known to provide information on the dynamical magnetic properties. Figure 4 shows the $T$ dependence of $1/T_1T$, which obeys the relation $1/T_1T=2073/(T-106)+49$ s$^{-1}$K$^{-1}$, in the metallic phase of $K_2V_8O_{16}$. In the 3d transition metals, $1/T_1T$ is expressed as $1/T_1T=(1/T_1T)_d+(1/T_1T)_{orb}$ where $(1/T_1T)_d$ and $(1/T_1T)_{orb}$ are due to the spin and orbital fluctuations, respectively. The orbital term is generally independent of $T$, whereas the spin term shows the $T$ dependence governed by the electron correlation. Thus the observed CW and constant terms are concluded to come from the spin and orbital fluctuations, respectively. The positive Weiss temperature in the CW term of $1/T_1T$, which is nearly equal to that of $K$, shows the presence of the ferromagnetic fluctuations which are supported by the theoretical study of the orbital ordering [12]. This is in contradiction.
Figure 4. Temperature dependence of $1/T_1 T$ in the metallic phase of $K_2V_8O_{16}$. The solid curve represents the fitted result of the data to the relation $1/T_1 T = A/(T - \Theta) + B$ where the $A$, $B$, and $\Theta$ are the fitting parameters.

to the results of $1/T_1$ obeying the modified Korringa relation with the antiferromagnetic spin fluctuations observed in $Bi_{1.77}V_8O_{16}$ and the Korringa relation in $Bi_{1.60}V_8O_{16}$ [8, 9, 10]. The difference between the spin dynamics in $K_2V_8O_{16}$ and the Bi oxides is considered to come from the difference of the electron number and the density of states at the Fermi level.

4. Conclusion
We have made $^{51}$V NMR measurements to study the metal-insulator transition and the local magnetic properties of the vanadium oxide with the Hollandite structure $K_2V_8O_{16}$ which undergoes the metal-insulator transition at $\sim 170$ K. An asymmetric $^{51}$V NMR spectrum observed in the metallic phase was found to have the $T$-dependent negative Knight shift and two spectra was observed around $T_{MI}$ due to the two-step first-order MI transition. The presence of the ferromagnetic fluctuations in the metallic phase was concluded from the $T$ dependence of $K$ and the $^{51}$V nuclear spin-lattice relaxation rate $1/T_1$. In the insulating phase, we observed the NMR spectrum with $K \sim 0.35\%$, indicating the presence of the nonmagnetic ground state.

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References
[1] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. 70 1039
[2] Yamada H and Ueda Y 1999 J. Phys. Soc. Jpn. 68 2735
[3] Itoh M, Akimoto N, Yamada H, Isobe M and Ueda Y 2000 J. Phys. Soc. Jpn. Suppl. B 69 155
[4] Suzuki T, Yamauchi I, Itoh M, Yamauchi T and Ueda Y 2006 Phys. Rev. B 73 224421
[5] Itoh M, Yamauchi I, Kozuka T, Suzuki T, Yamauchi T, Yamaura J and Ueda Y 2006 Phys. Rev. B 74 054434
[6] Yamauchi T and Ueda Y 2008 Phys. Rev. B 77 104529
[7] Yamauchi T, Ueda H, Yamaura J and Ueda Y 2007 Phys. Rev. B 75 014437
[8] Kato H, Waki T, Kato M, Yoshimura K and Kosuge K 2001 J. Phys. Soc. Jpn. 70 325
[9] Waki T, Morimoto Y, Kato H, Kato M and Yoshimura K, 2003 Physica B 329-333 938
[10] Waki T, Kato H, Kato M and Yoshimura K 2004 J. Phys. Soc. Jpn. 73 275
[11] Isobe M, Koishi S, Kouno N, Yamaura J, Yamauchi T, Ueda H, Gotou H, Yagi T and Ueda Y 2006 J. Phys. Soc. Jpn. 75 073801
[12] Horiuchi S, Shirakawa T and Ohta Y 2008 Phys. Rev. B 77 155120