Magnetic interactions and orbital state in double chain systems investigated by NMR measurements

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Abstract. We have made NMR measurements to clarify the relationship between the orbital state and the magnetic properties of the double chain compounds NaV$_2$O$_4$ and K$_2$Cr$_8$O$_{16}$. In both the oxides, the $t_{2g}$ orbital is split into a non-degenerated $d_{xy}$ and a degenerated $d_{yz;zx}$ orbital due to the lattice symmetry. Based on the anisotropy of the hyperfine coupling tensor determined by the present NMR measurements, we conclude the predominant $d_{xy}$ orbital and the partially occupied $d_{yz;zx}$ orbital, naturally leading to the double exchange mechanism of the ferromagnetic interaction. In addition to the ferromagnetic interaction, there is an antiferromagnetic interaction via the direct $d_{xy}$-$d_{xy}$ path along the double chain direction. Thus, the ferromagnetic transition takes place in K$_2$Cr$_8$O$_{16}$, whereas the helical spin order appears in NaV$_2$O$_4$ due to the competition between the ferromagnetic and antiferromagnetic interactions.

1. Introduction

Itinerant electron systems on a geometrically frustrated lattice with a triangular, pyrochlore or spinel structure show a variety of fascinating phenomena near the metal-insulator (MI) transition such as charge order with a spin-single ground state, heavy-mass Fermi liquid and superconductivity [1]. Recently, quasi-one-dimensional (quasi-1D) oxides with the calcium ferrite AM$_2$O$_4$ ($A$: alkali metal; $M$: transition metal) and the hollandite $A_2M_8O_{16}$ structures as shown in Figs. 1 (a) and (b), respectively, have been intensively investigated as a new frustrated quasi-1D system with a double chain shown in Fig. 1 (c) [2, 3, 4, 5, 6]. Among them, NaV$_2$O$_4$ with the mixed valence of V$^{3+}$:V$^{4+}$=1:1 (the average electron number 3$d^{1.5}$) was reported to be an antiferromagnetic (AFM) metal with $T_N$=140 K in spite of the strong ferromagnetic (FM) correlation which appears in magnetic susceptibility [4, 5] and the Knight shift [7]. Also an incommensurate helical spin structure was proposed in the AFM phase [8, 9]. A novel MI transition from the FM metallic to the FM insulating phases was reported to take place at $T_{MI}$=95 K in the FM state below $T_C$=180 K in K$_2$Cr$_8$O$_{16}$ with a rare mixed valence of Cr$^{3+}$:Cr$^{4+}$=2:6 (3$d^{2.25}$) [6]. In particular, the mechanism of the MI transition has attracted much attention from the experimental and theoretical point of views [6, 10]. In both oxides,
the orbital degree of freedom plays an important role for the magnetic and electric properties. As shown in Fig. 1 (d), the $t_{2g}$ orbital is considered to be split into a non-degenerated $d_{xy}$ and a degenerated $d_{yz,xz}$ ($d_{yz}, d_{zx}$) orbital due to the local symmetry. However, the orbital state and the frustration effect on the magnetic properties have not been understood clearly in the frustrated double chain systems.

In this study, we have performed $^{51}$V and $^{53}$Cr NMR measurements to study the orbital state and the magnetic interactions in NaV$_2$O$_4$ and K$_2$Cr$_8$O$_{16}$. We determine the hyperfine coupling constant $A$ and show that the ratio of the axially anisotropic to isotropic components, $A_{ax}/A_{iso}$, is a useful measure of the 3$d$ electron occupation number. The magnetic interactions in the double chain are discussed on the basis of the $t_{2g}$ orbital, and the competition between the FM and AFM interactions is concluded to play an important role for the helical spin order in NaV$_2$O$_4$ and the ferromagnetic order in K$_2$Cr$_8$O$_{16}$.

2. Experiments

A single crystal of NaV$_2$O$_4$ and a polycrystalline sample of K$_2$Cr$_8$O$_{16}$ were prepared for the present NMR measurements as reported in Refs. [5], and [6], respectively. $^{51}$V and $^{53}$Cr Fourier-transformed (FT) NMR spectra were measured in a magnetic field of $H_0 = 5.8701$ or 0.5 T by using a pulsed spectrometer. The $^{51}$V Knight shift was determined as $^{51}K=\nu_{res}-\nu_0)/\nu_0$ where $\nu_{res}$ is the $^{51}$V resonance frequency in the NaV$_2$O$_4$ sample and $\nu_0$ (=65.704 MHz) is that of the aqueous NaVO$_3$ solution measured at 5.8701T. Frequency-swept $^{53}$Cr NMR spectra in K$_2$Cr$_8$O$_{16}$ were taken point by point at 4.2 K and 0.5 T.

3. Results and discussion

In order to determine the angular dependence of the $^{51}$V Knight shift $^{51}K$ in NaV$_2$O$_4$, we made $^{51}$V NMR measurements with the single crystal rotated in $H_0 = 5.8701$ T. We observed two NMR spectra with no electric quadrupole splitting from the V1 and V2 sites, which are crystallographically inequivalent V sites in the orthorhombic lattice (space group Pnma), and each spectrum with $H_0$ applied in the $ca$ plane was furthermore split into two spectra due to the
local symmetry axes different from each other at the V sites on the mirror plane perpendicular to the b axis [11]. Also the angle range where the spectrum can be observed was limited due to anisotropy of the nuclear spin-spin relaxation time $T_2$. Figures 2 (a)-(c) show the angular dependence of $^{51}K$ at 260 K in the $bc$, $ca$, and $ab$ planes, respectively. The angular dependence in the $bc$ plane is well fitted to the equation $^{51}K = k_1 + k_2 \cos 2\theta_a + k_3 \sin 2\theta_a$ where $k_1$, $k_2$, and $k_3$ are the fitting parameters including Knight shift components expressed in the $abc$ coordinate system and $\theta_a$ is the angle between the $b$ axis and $H_0$ [12], as shown by the solid and dotted curves in Fig. 2 (a). The equations for the $H_0$ rotation in the $ca$ and $ab$ planes are obtained by cyclic permutation. After diagonalizing the Knight shift tensor in the $abc$ coordinate system, we obtain the $X$, $Y$, and $Z$ principle components of the shift tensor as $(^{51}K_X, ^{51}K_Y, ^{51}K_Z) = (-4.0, -4.3, -6.9\%)$ at 260 K for the V1 site and $(-3.7, -3.8, -5.4\%)$ for the V2 site.

In 3$d$ transition metal oxides, the Knight shift is generally composed of the orbital and spin parts as $K = K_{\text{spin}} + K_{\text{orb}}$, and magnetic susceptibility $\chi$ is similarly composed of the orbital, spin, and diamagnetic ones as $\chi = \chi_{\text{spin}} + \chi_{\text{orb}} + \chi_{\text{dia}}$ where $\chi_{\text{dia}} = -3.5 \times 10^{-5}$ emu/V mol [13] for NaV$_2$O$_4$. Also $K_{\text{spin}}$ is expressed as $K_{\text{spin}} = A \chi_{\text{spin}} \mu_B$ where $A$ is the hyperfine coupling constant, $N_A$ is the Avogadro’s number and $\mu_B$ is the Bohr magneton. From the standard analysis of the $^{51}K$ versus $\chi$ plots in NaV$_2$O$_4$ as shown in Fig. 2(d), we obtain the principal values of the hyperfine coupling tensor as $(^{51}A_X, ^{51}A_Y, ^{51}A_Z) = (-81, -87, -150)$ for the V1
site and (−66, −64, −100) in the units of kOe/μB for V2. The result of $^{51}A_X \sim ^{51}A_Y$ supports the presence of the degenerate $d_{zx,zz}$ orbital.

The Knight shift and hyperfine coupling tensors governed by the magnetic hyperfine interaction $\mathcal{H}_{\text{mag}}$ are useful to study the electron orbital in 3d transition metal oxides. In general, $\mathcal{H}_{\text{mag}}$ is expressed as

$$\mathcal{H}_{\text{mag}} = -2\mu_B^2 \gamma_n \hbar \langle r^{-3} \rangle_{\text{mag}} [\kappa \mathbf{S} \cdot \mathbf{I} - L \cdot I + \xi \mathbf{S} \cdot \mathbf{q} \cdot \mathbf{I}],$$  

where $\gamma_n$ is the nuclear gyromagnetic ratio, $\hbar$ the Planck’s constant, $\langle r^{-3} \rangle_{\text{mag}}$ the expectation value of $r^{-3}$ for the 3d orbital, $\kappa$ a parameter for the Fermi contact interaction due to the core-polarization effect, $\mathbf{S}$ the total electron spin, $\mathbf{L}$ the total orbital momentum, and $\mathbf{I}$ the nuclear spin operator. Also $\xi = \frac{2(1+4S)}{5S(2S-1)(2S+1)}(l=2$, $S=1/2$, and $L=2$ for $3d^5$) and $\mathbf{q}$ is the electron quadrupole moment tensor defined as $q_{n\alpha \beta} = \frac{1}{2} (L_n L_\beta + L_\beta L_n) - \delta_{n\alpha \beta} L^2 (\alpha, \beta = x, y, z)$ [14, 15].

The first term of eq.(1) is the Fermi contact interaction, the second is the orbital one, and the third is the dipole one. The anisotropy of the Knight shift tensor is mainly governed by the dipole interaction. For example, for $d_{zy}^2$, the expectation value of $\mathbf{q}$, which is proportional to the anisotropic part of the Knight shift tensor, is expressed as $(q_{xx}, q_{yy}, q_{zz}) = -3(1, 1, -2)$ where the $z$ axis of $\mathbf{q}$ is parallel to the symmetric axis of the $d_{zy}$ orbital, closely related to the principal axis of the Knight shift tensor. In NaV$_2$O$_4$, the $Z$ axis of the $^{51}$V Knight shift tensor is parallel to the direction to the apical oxygen of VO$_6$ octahedron as seen in Fig.1 (d). This is consistent with the local symmetry leading to the splitting of the 3d orbital to the non-degenerate $d_{xy}$ and the degenerated $d_{yz,zz}$ orbital.

We discuss the 3d electron occupation number from a ratio $A_{ax}/A_{iso}$ where $A_{iso}$ and $A_{ax}$ are isotropic and axial hyperfine coupling constants defined as $A_{iso}=(A_X + A_Y + A_Z)/3$ and $A_{ax}=(2A_Z - A_Y - A_X)/6$, respectively. Theoretically $A_{ax}/A_{iso} = \frac{2}{3} = 0.57$ for $d_{xy}$ and $-\frac{1}{3} = -0.29$ for $(d_{yz}^2 + d_{zx}^2)/2$ for a standard $\kappa = 0.5$. Comparing these values with the experimental value of $^{51}A_{ax}/^{51}A_{iso} \sim 0.2$, the ratio of the electron number $n_i$ ($i = xy, yz,$ and $zx$) on the $d_i$ orbital is estimated as $n_{xy}: n_{yz}: n_{zx} = 0.85: 0.32: 0.32$, showing the predominant occupied $d_{xy}$ orbital. Recently the band calculation in the generalized gradient approximation was made for the hollandite oxide K$_2$V$_8$O$_{16}$ with the similar crystal structure to that of NaV$_2$O$_4$ [16]. Based on the band calculation, they proposed a picture of the relatively localized $d_{xy}$ and itinerant $d_{yz}/d_{zx}$ electrons. This picture is applicable to NaV$_2$O$_4$ as discussed above on the occupation number, reasonably resulting in the double exchange mechanism as the origin of the ferromagnetic interaction which was observed by the magnetic susceptibility [4] and the NMR [7] experiments of NaV$_2$O$_4$.

In the paramagnetic state of K$_2$Cr$_8$O$_{16}$, the poor signal to noise ratio due to the small natural abundance of 9.5% prevented us from observing a $^{53}$Cr NMR spectrum. However, we could observe the $^{53}$Cr NMR spectrum in the ferromagnetic insulating phase below 95 K for the powdered sample. In a ferromagnetically ordered state, one usually observes NMR signals from domain and domain wall in $H_0 = 0$ T, whereas only the domain spectrum is observed above a magnetic field, ~0.5 T at 5 K in K$_2$Cr$_8$O$_{16}$ [6], where magnetization is saturated and becomes parallel to $H_0$. Figure 3 shows the $^{53}$Cr domain spectrum at 4.2 K and 0.5 T in K$_2$Cr$_8$O$_{16}$. It has no electric quadrupole splitting which is consistent with the small electric quadrupole frequency $\nu_{Q} < 1$ MHz reported in Cr compounds [17]. Thus the spectrum is governed by the internal field $H_{int} = 53AM$ due to the spontaneous magnetization $M$. In the ferromagnetic phase of K$_2$Cr$_8$O$_{16}$, the $^{53}$Cr NMR frequency $\nu$ is expressed as $\nu = \frac{g\mu}{h} \mathbf{M} \cdot \mathbf{H}$, where $53g = 2\pi \times 2.406$ MHz/T and $M | H_0 > 0.5$ T. The observed spectrum is well reproduced by assuming two powdered spectra with $^{53}A_{iso}, ^{53}A_{ax}, ^{53}A_{aniso} = (−92, −8.2, −6.1)$ for the Cr1 spectrum, where $A_{aniso}$ is defined as $A_{aniso} = (A_Y - A_X)/2$, and $(−82, −9.2, −8.2)$ in the units of kOe/μB for Cr2,
and the saturation moment $M = 2.21\mu_B$ [6] as shown in Fig. 3. The observation of the two spectra and $^{53}A_{\text{aniso}}$ indicates that the lattice symmetry in the ferromagnetic insulating phase lowers from the tetragonal one (space group $I4/m$) in the paramagnetic metallic phase. Also the ratio $^{53}A_{\text{aniso}}/^{53}A_{\text{iso}}$~0.1 shows the $d_{yz, zx}$ orbital more occupied than that in NaV$_2$O$_4$. This is consistent with the result of the first principle electronic calculation by Sakamai et al. [10]. They also found the rather dispersionless narrow band of predominantly $d_{xy}$ and the dispersive $t_{2g}$ bands of predominantly $d_{yz}$ and $d_{zx}$ character with strong admixture of the $2p_z$ of the oxygen and proposed the double exchange FM mechanism in K$_2$Cr$_8$O$_{16}$ [10].

Finally we discuss the magnetic properties of NaV$_2$O$_4$ and K$_2$Cr$_8$O$_{16}$. In these double chain systems, the FM interaction is ascribed to the double exchange mechanism via the $d_{yz}/d_{zx}$ orbital along the rung directions in the double chain as discussed above. In addition to the double exchange, an AFM interaction is expected to exist due to the direct $d_{xy}$-$d_{xy}$ path along the double-chain direction. Consequently there should appear the competition between the FM and AFM interactions. Indeed, NaV$_2$O$_4$ shows the helical spin order [8, 9] which comes from this competition as reported in double chain spin systems with the competing nearest and second nearest exchange couplings, $J_1$ and $J_2$, respectively, where a helical spin order appears for the ratio $|J_2/J_1|>1/4$ [18]. On the other hand, in K$_2$Cr$_8$O$_{16}$, the FM interaction is considered to overcome the AFM one, resulting in the FM spin order. The dominant FM double exchange interaction may be ascribed to the strong hybridization between the oxygen and chromium ions which makes the degenerate $d_{yz, zx}$ band width broader, as discussed in a negative charge transferred oxide CrO$_2$ [19].

4. Conclusion
We have performed $^{51}$V and $^{53}$Cr NMR measurements to investigate the local magnetic properties and the orbital state in the double chain systems NaV$_2$O$_4$ and K$_2$Cr$_8$O$_{16}$. From the analysis of the hyperfine coupling constant, we concluded that the 3$d$ electron occupation of the $d_{xy}$ orbital is predominant compared with that of the degenerated orbital $d_{yz, zx}$ orbital in both oxides, reasonably leading to the double exchange ferromagnetic interaction. The competition between the ferromagnetic interaction along the rung directions and the antiferromagnetic one
along the leg of the double chain direction plays an important role for the helical spin order in NaV$_2$O$_4$, whereas the predominant double exchange interaction results in the ferromagnetic order in K$_2$Cr$_8$O$_{16}$.

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**References**

[1] Gardner J S, Gingras M J and Greedan J E 2010 *Rev. Mod. Phys.* 82 53.

[2] Isobe M, Koishi S, Kouno N, Yamaura J, Yamauchi T, Ueda H, Goutou H, Yagi T and Ueda Y 2006 *J. Phys. Soc. Jpn.* 75 073801.

[3] Horiuchi S, Shirakawa T and Ohta Y 2008 *Phys. Rev. B* 77 155120.

[4] Yamaura K, Arai M, Sato A, Karki A B, Young D P, Movshovich R, Okamoto S, Mandrus D and Takayama-Muromachi E 2007 *Phys. Rev. Lett.* 99 196601.

[5] Sakurai H 2008 *Phys. Rev. B* 78 094410.

[6] Hasegawa K, Isobe M, Yamauchi. T, Ueda H, Yamaura J, Gotou H, Yagi T, Sato H and Ueda Y 2009 *Phys. Rev. Lett.* 103 146403.

[7] Takeda H, Itoh M and Sakurai H 2010 *J. Phys.: Conf. Ser.* 200 012200.

[8] Ofer O, Ikeda Y, Goko T, Mansson M, Sugiyama J, Ansaido E J, Brewer J H, Chow K H and Sakurai H 2010 *Phys. Rev. B* 82 094410.

[9] Takeda H, Itoh M and Sakurai H (unpublished).

[10] Sakamaki M, Konishi T and Ohta Y 2009 *Phys. Rev. B* 80 024416.

[11] Hahn Th (ed) 2002 *International Table for Crystallography* (Dordrecht : Kluwer Academic) vol A.

[12] Volkoff G M, Petch H E and Smellie D W 1952 *Can. J. Phys.* 30 270.

[13] Hellwege K H and Hellwege A M (ed) 1986 *Atomic and Molecular Physics* (Berlin: Springer) Landolt-Börnstein New Series Group II vol 16.

[14] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance in Transition Ions* (Oxford : Clarendon Press).

[15] Kiyama T and Itoh M 2003 *Phys. Rev. Lett.* 91 167202.

[16] Sakamaki M, Horiuchi S, Konishi T and Ohta Y arXiv:0811.4338.

[17] Narath A 1965 *Phys. Rev.* 140 A854.

[18] Bursill R, Gehring G A, Farnell D J J, Parkinson J B, Xiang T and Zeng C 1995 *J. Phys.: Condens. Matter* 7 8605.

[19] Korotin M A, Anisimov V I, Khomskii D I and Sawatzky G A 1998 *Phys. Rev. Lett.* 80 4305.