

## Microscopic Evidences of Bipolarons in the Quasi-One-Dimensional Conductor $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$

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The electronic states of the  $\text{V}^{4+}$  ions in  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  are studied by NMR and EPR measurements. The anomalous temperature dependence of the Knight shift of the  $^{51}\text{V}$  nuclei in site I can be understood by the spin singlet ground state of the electron pairs of the adjacent  $\text{V}^{4+}$  ions (bipolarons). Recent X-ray diffraction measurements reveal that this paired state is accompanied with the small ionic displacement, as predicted by Chakraverty *et al.* and the long range ordering of the bipolaronic state in the real space occurs below 200 K. From analyses of the anisotropic Knight shift and the quadrupole interaction, the electron wave function of the  $\text{V}^{4+}$  ions in site I is found to be mainly made of the  $d_{yz}$ -orbitals. The EPR results show that there are two components of the spin states: the bipolaronic spin singlet and the dilute isolated paramagnetic states.

### §1. Introduction

The physical properties of the nonstoichiometric compounds of  $\text{M}_x\text{V}_2\text{O}_5$  ( $\text{M}=\text{Li}, \text{Na}, \text{Cu}, \dots$ ) have been studied intensively since the discovery that  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ , the most typical material in this family, is one of the new quasi-one-dimensional conductors.<sup>1)</sup>

In the  $\beta$ -phase of  $\text{M}_x\text{V}_2\text{O}_5$ , there are three inequivalent crystallographic sites for the vanadium atoms,<sup>2,3)</sup> which are situated at the center of a deformed octahedron of the oxygen atoms and these make complex ladders extending along the monoclinic  $b$ -axis, the highest conductivity axis. The metal ions  $\text{M}$  are accommodated in tunnels of the oxygen atoms running parallel to the  $b$ -axis. The outer shell electrons of the  $\text{M}$  ions transfer into the unfilled  $d$ -shell of the vanadium ions incompletely; consequently the vanadium ions are expected to be in the mixed valence states of the  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions. The origin of the high and anisotropic conductivity is considered to be due to an electron hopping in the zigzag chains of the vanadium ions along the  $b$ -axis.

In case of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ , the vanadium ions in site I, their number being 0.67 per molecule, are occupied by most of the donated

0.33 electrons;<sup>4)</sup> that is, they are in a 1:1 mixture of the  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions. With respect to the dynamical behaviors of the  $3d$ -electrons, the correlation time of an electron hopping motion along the vanadium chains in site I at 77 K is estimated to be less than  $10^{-11}$  s from an analysis of NMR spin-lattice relaxation of the  $^{23}\text{Na}$  nuclei.<sup>5)</sup> The EPR results<sup>6)</sup> at 77 K proposed the model that the electrons at the adjacent  $\text{V}^{4+}$  ions in the vanadium chains in site I are coupled as pairs.

NMR measurements<sup>7)</sup> established that this material undergoes a first-order structural phase transition between 130 and 170 K by the observation of a jump of the  $^{51}\text{V}$  satellite position due to the nuclear quadrupole effect. Recently, a set of satellite reflections by X-ray diffraction measurements<sup>8)</sup> were observed with the wave vector of  $(0, 0.5, 0)$  below 200 K, which means that the period of the superstructure is twice the lattice constant along the  $b$ -axis. This phase transition is considered to be caused by the long range ordering of a dimerization of the  $\text{V}^{4+}$  pairs in site I due to the interionic attractive force.

The purpose of the present paper is to make clear the electronic states of the  $\text{V}^{4+}$  ions in site I, since it is expected to be primarily important to understand the physical properties of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ . In the present work, we found the Knight shift maximum phenomena

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of the  $^{51}\text{V}$  nuclei in site I. This result was understood by the spin singlet ground state of the  $\text{V}^{4+}$  pairs, we may call this state the bipolaronic one, which was proposed by Chakraverty *et al.*<sup>9)</sup> Moreover, we determined the energy level configuration of the  $3d$ -electrons as well as the electron wave function in the bipolaronic  $\text{V}^{4+}$  state. Recently, the bipolaronic state, formed by the strong electron-phonon interaction in narrow-band crystals, has been discussed theoretically.<sup>10,11)</sup>

## §2. Experimental

Single crystals of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  were prepared by Bridgman method from the melt of a 1:6 molar mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{V}_2\text{O}_5$  powder in air atmosphere. The sample for NMR measurements was made by stacking a number of single crystals with a typical size of  $0.5 \times 10 \times 0.1 \text{ mm}^3$ , and that for EPR measurements was small single crystals with a typical size of  $1 \times 2 \times 0.1 \text{ mm}^3$ .

NMR measurements were carried out by using a crossed-coil method with a Varian continuous-wave NMR spectrometer at a frequency of 22 MHz in the temperature range between 77 and 295 K. At 77 and 290 K, the frequency from 10 to 20 MHz was used to determine the nuclear quadrupole interaction parameters. The external field was calibrated by measuring the  $^{23}\text{Na}$  and  $^{51}\text{V}$  resonance signals in aqueous  $\text{NaVO}_3$  solution, especially the  $^{51}\text{V}$  resonance signal was used as a reference position of zero resonance shift. The temperature at the sample in NMR probe was controlled by a gas flow system of chilled nitrogen with a regulated current through electric heater. A Pt-resistance temperature sensor near the sample monitored the temperature of gas stream and regulated it to an accuracy of 1 K. A liquid nitrogen dewar was used for the measurements at 77 K.

The EPR absorption spectra were obtained by using a standard X-band spectrometer JEOL JES-FE 3X in the temperature range between 19 and 307 K. The temperature at the sample was varied and controlled with an Air Products Heli-tran temperature control system, and at 77 K a liquid nitrogen dewar was used.

## §3. Experimental Results

### 3.1 NMR results

We measured the  $^{51}\text{V}$  NMR spectra with spin  $I=7/2$  from 77 to 295 K, which contain the resonance lines from the vanadium atoms in sites I, II and III at the external field parallel to the  $b$ -axis. In the previous paper,<sup>4)</sup> we concluded that the resonance line having a large negative shift originates from the vanadium atoms in site I, by an analysis of the second-order quadrupole interaction. Table I shows the nuclear quadrupole interaction parameters of the vanadium atoms in site I, at 77 and 290 K; that is, the quadrupole frequency, the asymmetry parameter and the angle between the  $a$ -axis and the direction of the maximum electric field gradient, which are expressed by  $\nu_Q = 3e^2qQ/2I(2I-1)\hbar$ ,  $\eta = (V_{xx} - V_{yy})/V_{zz}$  and  $\Omega$ , respectively.<sup>12)</sup> Considering the effect of the second-order quadrupole interaction above and below the structural phase transition temperature, we obtained the temperature dependence of the Knight shifts of the vanadium atoms in site I at the external field parallel to the  $b$ -,  $a$ - and  $c^*$ -axes,\* as shown in Fig. 1.

Table I. The nuclear quadrupole interaction parameters of the vanadium atoms in site I at 77 and 290 K.

$T$ (K)	$\nu_Q$ (MHz)	$\eta$	$\Omega$
77	0.338	0.10	$67^\circ \pm 3^\circ$
290	0.278	0.30	$71^\circ \pm 4^\circ$

### 3.2 EPR results

The temperature dependence of the spin susceptibility is shown in Fig. 2, which is consistent with the published data by Friederich *et al.*<sup>13)</sup> within experimental accuracy. In addition to this, they measured the temperature dependence of the  $g$ -factor and the linewidth in a certain crystal orientation. In the present work, we concentrate on precise measurements of the anisotropy of the  $g$ -factor and the linewidth. Figure 3(a) and (b) shows the angular- and the temperature-dependence of the  $g$ -factor. The principal axes

\* The  $c^*$ -axis is perpendicular to the crystallographic  $a$ - and  $b$ -axes.

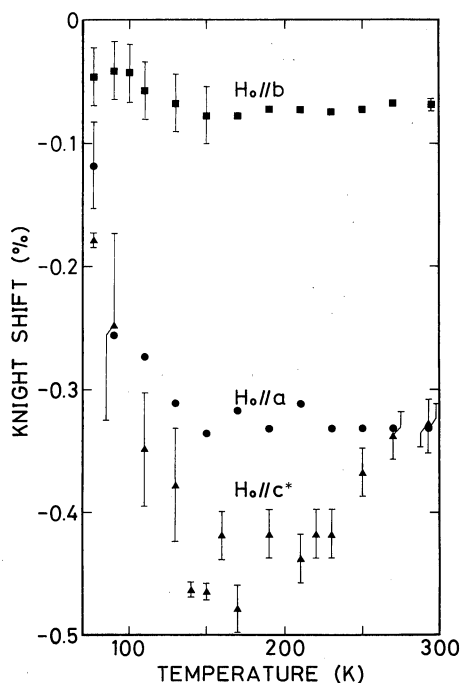


Fig. 1. Temperature dependence of the Knight shifts of the  $^{51}\text{V}$  nuclei in site I at the external field parallel to the  $a$ -,  $b$ - and  $c^*$ -axes.

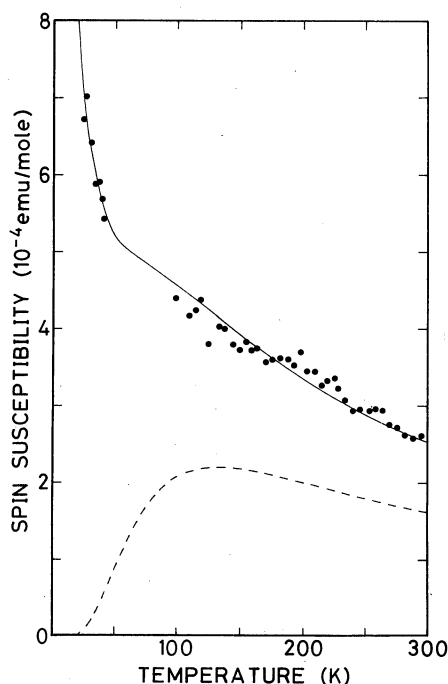


Fig. 2. Temperature dependence of the spin susceptibility. Solid and dashed lines show the calculated results obtained by using the formula and the parameters given in §4.3.

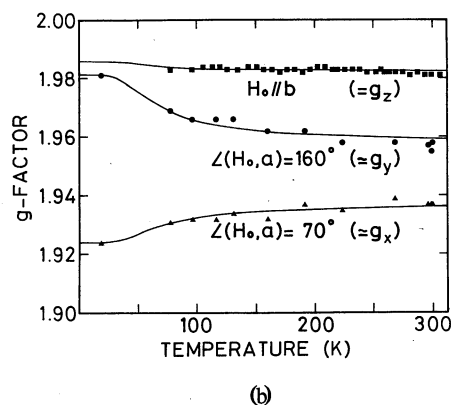
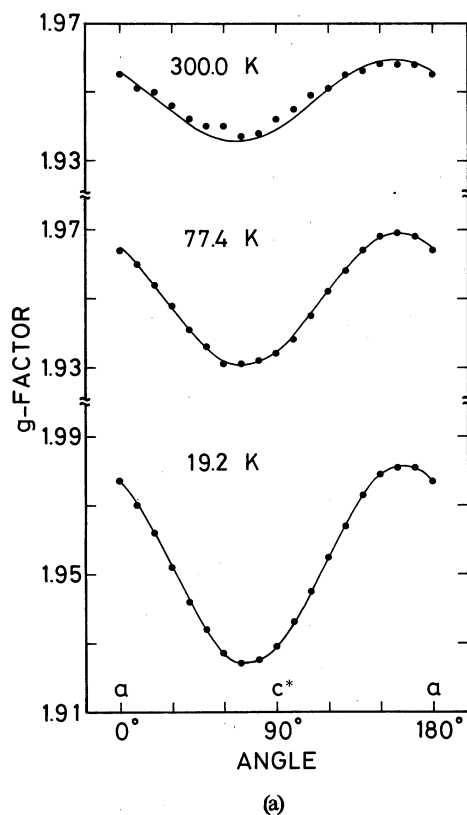


Fig. 3. (a) Angular dependence of the  $g$ -factor in the  $(a, c)$  plane at several temperature. (b) Temperature dependence of the  $g$ -factor. Solid lines show the calculated results by using the formula and the parameters given in §4.4.

$X$  and  $Y$  lie in the  $(a, c)$  plane and the  $Z$ -axis corresponds to the  $b$ -axis. The angle between the  $a$ -axis and the  $X$ -axis is about  $70^\circ$ . Figure 4(a) and (b) shows the angular- and the temperature-dependence of the apparent peak-to-peak linewidth of the absorption derivative at 9 GHz.

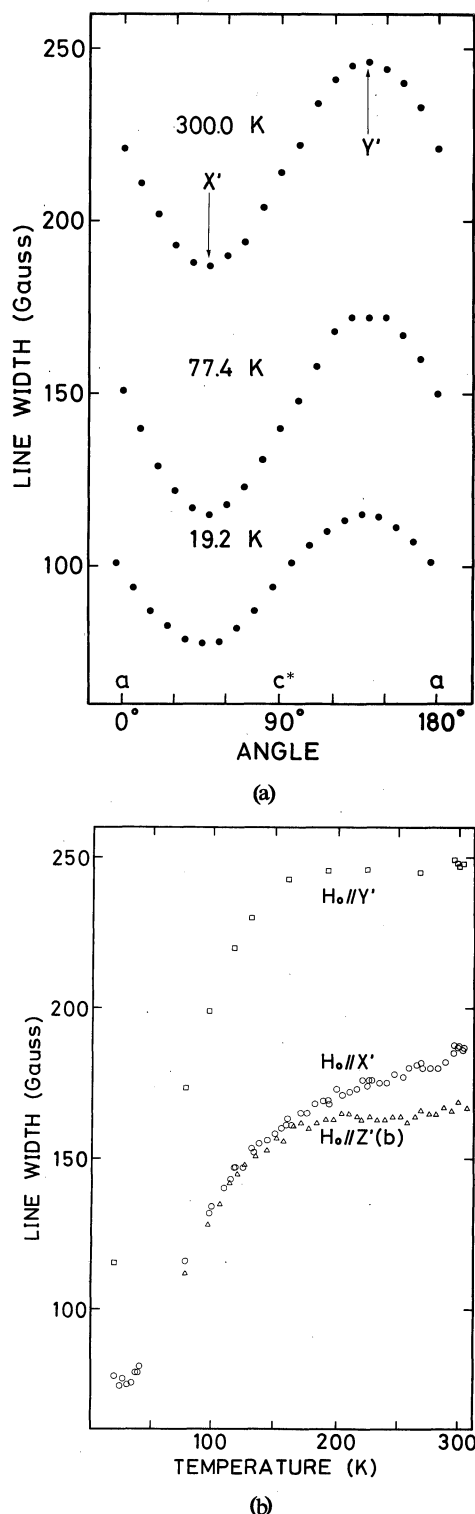


Fig. 4. (a) Angular dependence of the apparent peak-to-peak linewidth of the absorption derivative in the (a, c) plane at several temperature. (b) Temperature dependence of the apparent peak-to-peak linewidth of the absorption derivative.

## §4. Discussions

### 4.1 Knight shift

#### 4.1.1 Temperature dependence of the average Knight shift

In general, the Knight shift  $K(T)$  and the susceptibility  $\chi(T)$  can be written:<sup>14,15)</sup>

$$K(T) = K_s + K_{VV} + K_d(T), \quad (1)$$

$$\chi(T) = \chi_{dia} + \frac{2}{3}\chi_s + \chi_{VV} + \chi_d(T), \quad (2)$$

where  $K_s$  and  $\chi_s$  are the Knight shift and the susceptibility from the  $s$ -band electron contribution, respectively,  $K_{VV}$  and  $\chi_{VV}$  are those of the Van Vleck constant paramagnetism, and  $\chi_{dia}$  the closed-shell diamagnetic susceptibility making usually no contribution to  $K(T)$ . The temperature dependence of these terms is generally small and can be ignored. The temperature dependent term  $\chi_d(T)$  is the susceptibility of the  $d$ -electron spin, and the different contributions to  $K_d(T)$  are expressed by

$$K_d(T) = K_{cp}(T) + K_{dip}(T) + K_{orb}(T), \quad (3)$$

where  $K_{cp}(T)$ ,  $K_{dip}(T)$  and  $K_{orb}(T)$  are the Knight shifts from the inner-core polarization induced by the  $d$ -electron spin, the electron-nuclear spin dipole interaction and the  $d$ -orbital moment contributions, respectively. These contributions to  $K(T)$  are related to their respective susceptibilities by the following equation

$$K_i = \frac{1}{N_A \mu_B} H_{hf}^i \chi_i, \quad (4)$$

where  $N_A$  is Avogadro's number,  $\mu_B$  the Bohr magneton, and  $H_{hf}^i$  the hyperfine coupling field. Corresponding to eq. (3),  $H_{hf}^i$  is given as follows:

$$H_{hf}^d = H_{hf}^{cp} + H_{hf}^{dip} + H_{hf}^{orb}. \quad (5)$$

Although  $H_{hf}^s$  of the  $4s$ -electron is larger by an order of magnitude than  $H_{hf}^d$  of the  $3d$ -electron in usual  $3d$  transition metal,<sup>16)</sup> the  $4s$ -electron contribution  $K_s$  to  $K(T)$  can be ignored because  $\chi_s$  is negligibly smaller than  $\chi_{VV}$  and  $\chi_d(T)$  in  $\beta$ -Na<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub>.

Therefore, we can express the Knight shift of the <sup>51</sup>V nuclei as follows:

$$K(T) = K_{VV} + K_d(T) \\ = \frac{1}{N_A \mu_B} [H_{hf}^{VV} \chi_{VV} + H_{hf}^d \chi_d(T)]. \quad (6)$$

Since the vanadium atoms in site I are in a 1:1 mixed valence state of the  $V^{4+}$  and  $V^{5+}$  ions<sup>4)</sup> and there occur rapid valence fluctuations between them,<sup>5,6)</sup> the observed Knight shift is expected to be the average value. Thus we can express the average Knight shifts for  $j=a$ -,  $b$ - and  $c^*$ -axes as follows:

$$\begin{aligned}\langle K(T) \rangle_{AV} &= \frac{1}{3} \sum_j [K_{VV}^j + K_d^j(T)] \\ &= \langle K_{VV} \rangle_{AV} + \frac{1}{2N_A \mu_B} \langle H_{hf}^d \rangle_{AV} \chi_d(T),\end{aligned}\quad (7)$$

where  $\langle K_{VV} \rangle_{AV}$  denotes the average Van Vleck component in the mixed valence states.

The temperature dependence of  $\langle K(T) \rangle_{AV}$  is obtained by an empirical fit of the form<sup>9)</sup>

$$\begin{aligned}\langle K(T) \rangle_{AV} &= \langle K_{VV} \rangle_{AV} + \frac{g_0^2 \mu_B S(S+1)}{6k} \\ &\quad \times \langle H_{hf}^d \rangle_{AV} \frac{1}{T} \frac{e^{-\Delta/T}}{1 + e^{-\Delta/T}},\end{aligned}\quad (8)$$

where  $g_0 = 2.0023$ ,  $S = 1/2$ ,  $k$  is Boltzmann constant, and  $\Delta$  the binding energy for the bipolaronic state of the electron in the temperature scale. Here, we must evaluate  $\langle H_{hf}^d \rangle_{AV}$  in eq. (8). For the isotropic first term in eq. (5), Pouget *et al.*<sup>17,18)</sup> have obtained, for the  $V^{4+}$  ion in the octahedral oxygen environment of  $VO_2$ ,  $H_{hf}^{cp} = -83 \pm 3$  kOe/ $\mu_B$ . The average of the second term is zero and the third term, usually expressed as

$$H_{hf}^{orb} = (g - g_0) \mu_B \langle r^{-3} \rangle, \quad (9)$$

where  $g$  is the  $g$ -factor of EPR line and  $\langle r^{-3} \rangle$  the expectation value of  $r^{-3}$ . The electronic configuration of  $V^{4+}$  is  $(3d)^1$  and it is estimated that  $\langle r^{-3} \rangle = 3.684$  a.u. for the  $V^{4+}$  ion.<sup>16)</sup> Using the  $g$ -factor for the bipolaronic state listed in Table II (§4.4), we obtain  $\langle H_{hf}^{orb} \rangle_{AV} = -11$  kOe/ $\mu_B$ , and  $\langle H_{hf}^d \rangle_{AV}$  is estimated to be  $-94$  kOe/ $\mu_B$ . Then, the fit to eq. (8) shown in Fig. 5 by solid line is obtained for  $\Delta = 192$  K and  $\langle K_{VV} \rangle_{AV} = 0.164\%$ . The physical meaning of this fit is that the ground state of the  $3d$ -electrons of the  $V^{4+}$  ions in site I is nonmagnetic and the thermally excited state has a magnetic moment. Here, it should be noted that the similar analysis, based upon a singlet-triplet spin structure in the exchange coupled two spin system,<sup>18)</sup> is possible. But taking the high conductivity<sup>1)</sup> and the existence of the

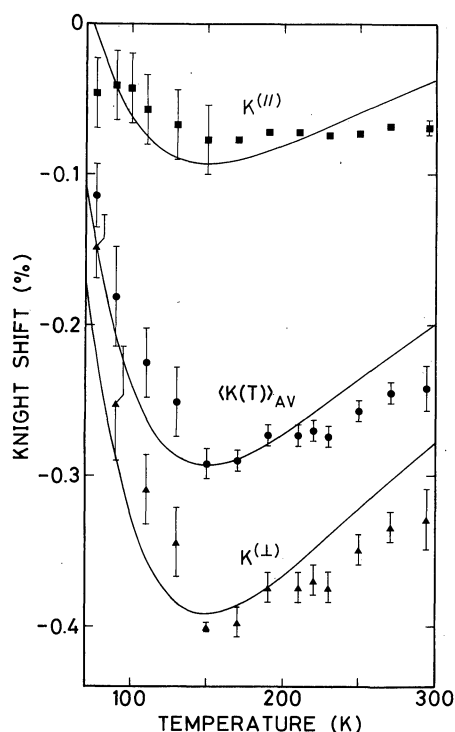


Fig. 5. Calculated temperature dependence of the average and the anisotropic Knight shifts of the  $^{51}\text{V}$  nuclei in site I compared with the experimental results. For the used formula and parameters, see text.

nonmagnetic  $V^{5+}$  ions<sup>4)</sup> along the  $b$ -axis in  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  into consideration, we chose a single polaronic state with spin  $S = 1/2$  as the excited state.

#### 4.1.2 Anisotropy of the temperature dependent Knight shift

The anisotropy of the temperature dependent Knight shift is originated by the magnetic field at a nucleus due to the electron-nuclear spin dipole interaction and the  $d$ -orbital moment.

The monoclinic  $b$ -axis is the axis of maximum symmetry in  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ .<sup>2,3)</sup> For simplicity, we introduce the Knight shift parameters as follows:  $K^{(//)} = K^b$ ,  $K^{(\perp)} = (K^a + K^{b*})/2$ , and their hyperfine coupling fields are defined by  $H_{hf}^{i(//)}$  and  $H_{hf}^{i(\perp)}$ , respectively. For the third term in eq. (5), we obtain  $H_{hf}^{orb(//)} = -5$  kOe/ $\mu_B$  and  $H_{hf}^{orb(\perp)} = -14$  kOe/ $\mu_B$  by using eq. (9) and the  $g$ -factor for the bipolaronic state listed in Table II. The second term in eq. (5) may be expressed in the tight-binding approximation<sup>19)</sup> as

$$H_{\text{hf}}^{\text{dip}} = \langle P_2^0(\cos \theta) \rangle \mu_B \langle r^{-3} \rangle P_2^0(\cos \Theta), \quad (10)$$

where  $P_2^0$  is associated Legendre function,  $\theta$  an angle between the electron position vector and the  $b$ -axis, and  $\Theta$  an angle between the external field and the  $b$ -axis. According to the structural data,<sup>2,3)</sup> the energy levels of the  $d_{\text{e}}$ -orbitals are considered to be lower than those of the  $d_{\gamma}$ -orbitals. Calculating eq. (10) for the  $d_{\text{e}}$ -orbitals of the  $d$ -electrons, we obtain the following results: For the  $d_{yz}$  and  $d_{zx}$ ,  $H_{\text{hf}}^{\text{dip}(\parallel)} = 32 \text{ kOe}/\mu_B$  and  $H_{\text{hf}}^{\text{dip}(\perp)} = -16 \text{ kOe}/\mu_B$ , for the  $d_{xy}$ ,  $H_{\text{hf}}^{\text{dip}(\parallel)} = -65 \text{ kOe}/\mu_B$  and  $H_{\text{hf}}^{\text{dip}(\perp)} = 32 \text{ kOe}/\mu_B$ , where the  $z$ -axis is parallel to the  $b$ -axis and the angle between the  $x$ -axis and the  $a$ -axis is about  $70^\circ$  for ideal octahedral sites.<sup>2,3)</sup> Comparing these calculated results with the experimental ones, we found that the ground state is made of either the  $d_{yz}$ - or  $d_{zx}$ -orbitals. Thus we obtain  $H_{\text{hf}}^{\text{d}(\parallel)} = -55 \text{ kOe}/\mu_B$  and  $H_{\text{hf}}^{\text{d}(\perp)} = -113 \text{ kOe}/\mu_B$ , and the best fits to eq. (8) with  $K_V^{(\parallel)} = 0.177\%$  and  $K_V^{(\perp)} = 0.159\%$ , as shown in Fig. 5 by solid lines. Here, we used  $H_{\text{hf}}^{\text{cp}} = -83 \text{ kOe}/\mu_B$  and  $\Delta = 192 \text{ K}$  obtained from the temperature dependence of  $\langle K(T) \rangle_{\text{AV}}$ . In spite of the rather simple discussions, the agreement is satisfactory.

#### 4.2 Quadrupole interaction

The electric field gradient  $q$  of the quadrupole frequency may usually be written:<sup>20)</sup>

$$q = q_{\text{latt}}(1 - \gamma_\infty) + q_{\text{loc}}(1 - R_Q), \quad (11)$$

where  $q_{\text{latt}}$  is the field gradient arising from the surrounding positive or negative ions,  $q_{\text{loc}}$  the contribution from the nonspherical distribution of the electrons in incomplete shell within the same  $V^{4+}$  ion to the  $^{51}\text{V}$  nuclei,  $\gamma_\infty$  and  $R_Q$  are the Sternheimer antishielding factors which express the contribution from the closed shells, distorted under the influence of the nonspherical potential and associated with  $q_{\text{latt}}$  and  $q_{\text{loc}}$ . Corresponding to eq. (11), the observed quadrupole frequency  $\nu_Q$  is expressed as follows:

$$\nu_Q = \nu_Q^{\text{latt}} + \nu_Q^{\text{loc}}. \quad (12)$$

The magnitude of  $\nu_Q^{\text{latt}}$  may be estimated by that of  $V_2O_5$ , in which the configuration of the nearest neighboring oxygen atoms around the vanadium ions<sup>21)</sup> is geometrically equivalent to the case of  $\beta\text{-Na}_{0.33}V_2O_5$ <sup>2,3)</sup> and the direction of the maximum electric field gradient

coincides with that of this material. The quadrupole frequency and the asymmetry parameter of  $V_2O_5$  are  $\nu_Q = 0.054 \text{ MHz}$  and  $\eta = 0$ , respectively.<sup>22)</sup> Thus we obtain  $\nu_Q^{\text{loc}} = 0.284 \text{ MHz}$  and  $0.1 < \eta_{\text{loc}} \leq 0.119$  at  $77 \text{ K}$ ,  $\nu_Q^{\text{loc}} = 0.224 \text{ MHz}$  and  $0.3 < \eta_{\text{loc}} \leq 0.372$  at  $290 \text{ K}$  from Table I. Here,  $\eta_{\text{loc}}$  is the asymmetry parameter corresponding to  $q_{\text{loc}}$ , and we assumed that  $(1 - \gamma_\infty)$ <sup>22)</sup> is equal to or larger than  $(1 - R_Q)$ .<sup>20)</sup>

Since the result of the anisotropic Knight shift analysis in §4.1.2 indicates that the ground state is made of either the  $d_{yz}$ - or  $d_{zx}$ -orbitals, we neglect the admixture of the  $d_{xy}$  in the ground state in the following discussions. Then,  $\eta_{\text{loc}}$  is easily expressed in the tight-binding approximation as

$$\eta_{\text{loc}} = \left| \frac{3(\zeta - 1)}{3\zeta - 1} \right|, \quad (13)$$

where  $\zeta$  and  $(1 - \zeta)$  are the amounts of the  $d_{yz}$ - and  $d_{zx}$ -orbitals at the Fermi level, respectively. On the basis of the experimental results and eq. (13), we get  $0.93 \leq \zeta < 0.94$  at  $77 \text{ K}$  and  $0.82 \leq \zeta < 0.85$  at  $290 \text{ K}$ . The ratio of  $\nu_Q^{\text{loc}}$  at  $77 \text{ K}$  to  $\nu_Q^{\text{loc}}$  at  $290 \text{ K}$  is  $1.20 \pm 0.05$  by using the values of  $\zeta$ . This ratio agrees well with  $0.284 \text{ MHz}/0.224 \text{ MHz} = 1.27$ . Therefore, we can conclude without ambiguity that the ground state is mainly made of the  $d_{yz}$ -orbitals. On the other hand, the electronic structure of  $\beta\text{-Na}_{0.33}V_2O_5$  has been discussed in detail by Goodenough<sup>23)</sup> in terms of the bond distances and the qualitative ligand field theory. According to his theory, the  $3d$ -electrons are localized to the  $d_{yz}$ -orbitals at the site I, which is consistent with our results.

#### 4.3 Spin susceptibility

The temperature dependence of the spin susceptibility can not be explained simply by the Curie-Weiss law and is different from that of the Knight shift as discussed in §4.1.

Since it is known that a certain kind of antiferromagnetic transition in  $\beta\text{-Na}_{0.33}V_2O_5$  occurs at about  $18 \text{ K}$ ,<sup>24)</sup> we suppose that the spin susceptibility is expressed by two components as follows:

$$\chi_d(T) = \chi_{\text{pair}}(T) + \chi_{\text{isolate}}(T), \quad (14)$$

where  $\chi_{\text{pair}}(T)$  is the susceptibility due to the paired electron in the spin singlet ground state, and  $\chi_{\text{isolate}}(T)$  is that due to the isolated para-

magnetic one. These susceptibilities are expressed<sup>9)</sup> by

$$\chi_{\text{pair}}(T) = \frac{C_p}{T} \frac{e^{-\Delta/T}}{1 + e^{-\Delta/T}}, \quad (15)$$

$$\chi_{\text{isolate}}(T) = \frac{C_i}{T + T_w}, \quad (16)$$

where  $C_p$  and  $C_i$  are the Curie constants, and  $T_w$  the Weiss temperature, estimated to be 18 K.<sup>24)</sup> The calculated results of  $\chi_d(T)$  and  $\chi_{\text{pair}}(T)$  given in eqs. (14)–(16) are shown in Fig. 2 by solid and dashed lines by using  $\Delta = 169$  K,  $T_w = 18$  K,  $C_p = 0.133 \pm 0.04$  emuK/mole,  $C_i = 0.029 \pm 0.009$  emuK/mole, respectively. This result indicates that the number of the isolated paramagnetic state is one fifth of the  $V^{4+}$  ions. In case of the complete transfer of the sodium electrons to the vanadium orbitals, the Curie constants in the susceptibility is expected to be 0.125 emuK/mole, so the obtained result agrees roughly with the expected value within large experimental error of 30% in the absolute value\* of the spin susceptibility. We can conclude that the sodium ion donates its electron to the vanadium orbitals completely on the basis of the absence of the sodium Knight shift<sup>7)</sup> and the present susceptibility results.

#### 4.4 $g$ -factor

We found that the observed spin susceptibility of  $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$  is composed of the spin singlet and the isolated paramagnetic states. So we can expect that the observed EPR lines are mixture of two resonance lines which have own  $g$ -factors and the linewidths. It was found that the difference of the  $g$ -factors between resonance lines is much smaller than the linewidth and the separation of the observed resonance line shape to two components at 9 GHz is unsuccessful. But at the measurements of a higher frequency of 35 GHz, the asymmetric resonance lines were observed. These results may be interpreted by the fact that the difference of the resonance field becomes greater at 35 GHz and comparable to the linewidth, and will be published by a

separate paper in future from the viewpoint of line shape analysis and relaxation phenomena.

In order to determine the each  $g$ -factor, we tried to analyze the average value of the  $g$ -factor. The average  $g$ -factor is given by the weighted mean of two  $g$ -factors as functions of temperature and an angle  $\phi$  between the external field and the crystal axis in the ( $a$ ,  $c$ ) plane:

$$g(T, \phi) = \frac{g_p(\phi)\chi_{\text{pair}}(T) + g_i(\phi)\chi_{\text{isolate}}(T)}{\chi_{\text{pair}}(T) + \chi_{\text{isolate}}(T)}, \quad (17)$$

where  $g_{p,i}(\phi)$  are the  $g$ -factors for  $\chi_{\text{pair},\text{isolate}}(T)$ . The best fits to eq. (17) shown in Fig. 3(a) and (b) by solid lines give the results as listed in Table II. For both  $g$ -factors, the principal axes  $X$  and  $Y$  lie in the ( $a$ ,  $c$ ) plane and the  $Z$ -axis corresponds to the  $b$ -axis. For  $g_i$ , the angle between the  $a$ -axis and the  $X$ -axis is about  $73^\circ$ . We consider the energy level configuration in the spin singlet ground state. The  $g$ -factor of  $(3d)^1$ -ions in nearly octahedral crystal field can be calculated by a simple perturbation theory of the spin-orbit coupling:<sup>25)</sup>

$$g_{ab} = g_0 \delta_{ab} - 2\lambda \sum_{n \neq 0} \frac{\langle 0 | L_a | n \rangle \langle n | L_b | 0 \rangle}{W_n - W_0}, \quad (18)$$

Table II. The  $g$ -factors for the bipolaronic spin singlet state ( $g_p$ ) and the dilute isolated paramagnetic one ( $g_i$ ).

	$X$	$Y$	$Z$
$g_p$	$1.944 \pm 0.004$	$1.944 \pm 0.004$	$1.981 \pm 0.002$
$g_i$	$1.982 \pm 0.002$	$1.924 \pm 0.002$	$1.986 \pm 0.002$

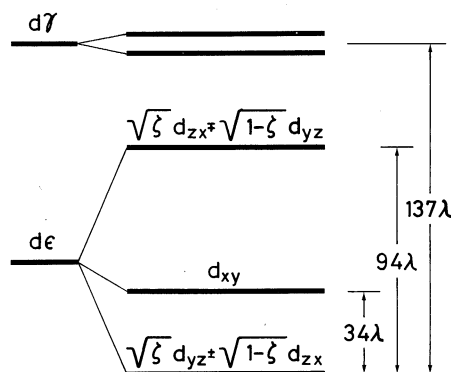


Fig. 6. Energy level configuration of the  $3d$ -orbitals in the bipolaronic  $V^{4+}$  state. Here,  $\zeta$  is the mixing parameter and  $\lambda$  is the spin-orbit coupling constant. In §4.2, the value of  $\zeta$  is determined as  $0.93 \leq \zeta < 0.94$  at 77 K and  $0.82 \leq \zeta < 0.85$  at 290 K.

\* The large ambiguity about the absolute value of the spin susceptibility is inevitable due to the choice of the reference signal and the size of the sample. In our case, we use  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as the reference signal and the typical size is  $1 \times 2 \times 0.1$  mm<sup>3</sup>.

where  $a, b = x, y, z$ ;  $\lambda$  is the spin-orbit coupling constant,  $L_a$  the orbital angular momentum operator, and  $W_n$  the energy of the orbital state  $n$ . We have already shown that the ground state is mainly made of the  $d_{yz}$ -orbitals in §4.2. Then, we found the energy level configuration that can explain the obtained anisotropy of the  $g$ -factor is as shown in Fig. 6. It is noteworthy that the  $g$ -factor for the isolated paramagnetic state agrees well with that of the dilute  $V^{4+}$  ions in  $V_2O_5$ .<sup>26,27)</sup>

## §5. Conclusion

The observed Knight shift maximum phenomena of the  $^{51}V$  nuclei in site I in  $\beta$ - $Na_{0.33}V_2O_5$  were found to be interpreted by the temperature dependence of the spin singlet ground state and the thermally excited magnetic state of the  $V^{4+}$  ions. On the other hand, recent X-ray diffraction measurements reveal that there occurs a dimerization of the vanadium ions below 200 K in this material. Therefore, it is concluded that the bipolaronic state, predicted by Chakraverty *et al.*, is realized as the spin singlet ground state of the electron pairs of the adjacent  $V^{4+}$ - $V^{4+}$  ions, accompanied with the small ionic displacement in  $\beta$ - $Na_{0.33}V_2O_5$ .

In the temperature dependence of the Knight shift of the  $^{51}V$  nuclei in site I and the spin susceptibility, no anomaly was observed around 200 K, below which the long range ordering of a dimerization of the  $V^{4+}$ - $V^{4+}$  ions in site I occurs. This result suggests that the short range dimerization already exists above 200 K.

On the basis of analyses of the anisotropic Knight shift and the quadrupole interaction, the electron wave function of the  $V^{4+}$  ions in site I was found to be mainly made of the  $d_{yz}$ -orbitals. It was shown that there are two components of the spin states: the bipolaronic spin singlet and the dilute isolated paramagnetic states, from the EPR results. The energy level configuration of the  $3d$ -orbitals in the bipolaronic  $V^{4+}$  state was determined.

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