# Spin ordering of $3d^1$ electrons shared within rungs in ladder-type vanadate $\beta$-$Ag_{0.33}V_2O_5$: Nuclear magnetic resonance and zero-field resonance measurements

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Spin ordering in $\beta$-$Ag_{0.33}V_2O_5$, a ladder-type pressure-induced superconductor, was observed from NMR and zero-field resonance (ZFR) at ambient pressure as an ordering of a $3d^1$ electron confined within a molecular orbital formed at two V sites on a rung.

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A series of $\beta$-$A_{0.33}V_2O_5$ ($A$=Li, Na, and Ag) has attracted much attention in strongly correlated electron systems because it is the first to exhibit superconductivity (SC) as a low dimensional vanadate.[1,2] System covalency is of two-leg ladder type according to a recent tight-binding calculation.[3] The system is electron doped and exhibits several phases although the electron density is low; superconductivity is realized under a pressure of over 6 GPa and a charge-ordered (CO) phase, followed by a magnetic ordering at low temperatures, emerges as a low-pressure phase adjacent to a superconducting phase.[4–6] A novel mechanism such as a charge-fluctuation induced mechanism is expected for the appearance of superconductivity.[7]

The paramagnetic CO phase is included in an insulating phase caused by a metal-insulator transition and is accompanied by lattice modulation with sixfold periodicity in the leg direction.[8,9] In the insulating phase, only one $3d^1$ electron exists per six V sites to maintain electrical neutrality; the series is formally expressed as $\beta$-$A_{0.33}(V^{4+}+5V^{5+})_{0.33}O_5$, where $V^{4+}$ is a magnetic ion with a $3d^1$ electron, and $V^{5+}$ is a nonmagnetic ion. In a simple CO picture, a $3d^1$ electron with spin $S=1/2$ would occupy one site among six sites.

In $\beta$-$Na_{0.33}V_2O_5$ several charge-distribution models have been presented by optical measurements, ESR, neutron scattering, and NMR measurements.[10–14] ESR measurements suggest a block-wise charge, and $3d^1$ electrons are mainly located on V1 sites among three crystallographically inequivalent sites Vi ($i$=1, 2, and 3).[11] Neutron-diffraction measurements suggest a charge model which contains nonmagnetic sites with three-lattice unit periodicity in the leg direction. Relative charge density for the Vi sites was estimated as 3:2:3, respectively.[12] $^{23}$Na-NMR measurements have been analyzed based on this model, and the density was estimated as 3:1:1 for the Vi sites, respectively.[13] There is no consensus on charge distribution and the above-mentioned simple CO model is not obvious.

There are two possibilities for a $3d^1$ electron occupying over several sites in an insulating state; one is formation of a charge density wave (CDW) caused by nesting of Fermi surface, and the other is charge sharing within several sites caused by the relationship between hopping and Coulomb repulsions between neighboring sites. The possibility of the charge sharing was suggested by the simulation in trellis-lattice structure.[14] The former and latter appear when the phonon-electron and electron-electron interactions play an important role, respectively. Paramagnetic state of $\alpha$-$NaV_2O_5$, a two-leg ladder with the valence of $V^{4.5+}$, is regarded as the real example for the latter case.[14,15]

In the present system the charge sharing within several sites seems possible rather than formation of the CDW because the insulating phase of $\beta$-$Sr_{0.33}V_2O_5$, an isomorphic $\beta$-vanadium bronze, is hardly explained by the nesting of Fermi surface; several pressure-induced insulating phases accompanied with superstructures were observed without the changes of crystal structure and carrier number.[16] It is unlikely that all of the phases arise from the nesting of Fermi surface because the crystal structure is unchanged. If the charge sharing is realized, what is the spin ordering like? The simplest case is a $3d^1$ electron shared within a rung like a hydrogen molecule; when $|i\rangle$ ($i$=1, *and* 2) represents the CO state where a $3d^1$ electron with up spin ($S^z=1/2$) is located on a site as shown in Fig. 1, a $3d^1$ electron shared within a rung is expressed as

$$|a\rangle = \frac{1}{\sqrt{2}}(|1\rangle + e^{i\theta}|2\rangle), \tag{1}$$

where $\theta$ is an arbitrary number, but the energy depends on its value, as do the charge densities; an appreciable energy difference can be expected between the bonding state ($\theta$=0) and the antibonding state ($\theta=\pi$). The occupation of the bonding state would have more charge in between the two V sites and lead to a strong coupling to phonons. This would locally favor a shortening of the rung. The expectation values of $S_i^z$,

$$\langle a|S_1^z|a\rangle = 1/4, \tag{2}$$

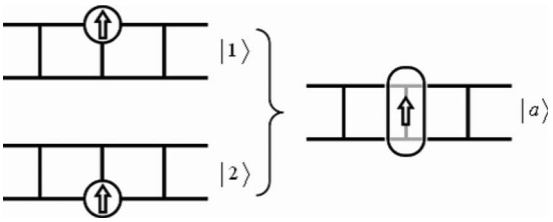


FIG. 1. Two states $|1\rangle$ and $|2\rangle$ represent CO states where a $3d^1$ electron with up spin is located on a site. A $3d^1$ electron shared within a rung is denoted as $|a\rangle$ in Eq. (1). The arrows in the figure represent spins with $S=1/2$.

 

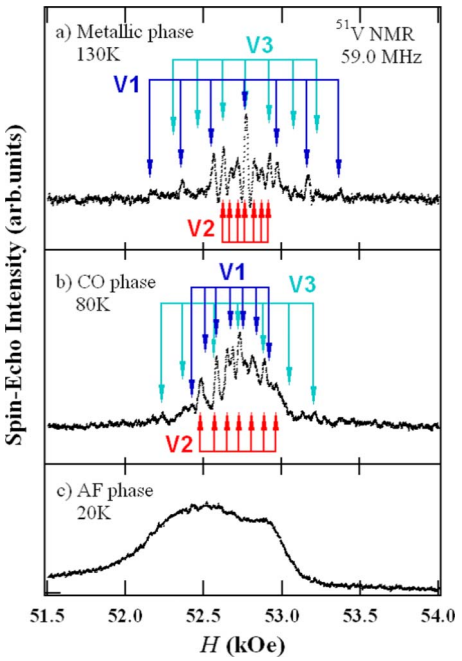


FIG. 2. (Color online) $^{51}$V-NMR spectra for the metallic, CO, and AF phases. The field $\boldsymbol{H}$ was applied to the $b$ axis, the leg direction. Site assignment was performed using the data obtained for the $\boldsymbol{H}$ parallel to the ac plane [see Fig. 3(b)].

$$\langle a|S_2^z|a\rangle = 1/4, \tag{3}$$

are derived from $S_i^z|j\rangle=(1/2)\delta_{ij}|j\rangle$ and $\langle i|j\rangle=\delta_{ij}$. Therefore, the charge sharing gives rise to a hyperfine field, at a nucleus site, of half the magnitude expected in the CO state where a $3d^1$ electron localizes at a single site. In $\alpha$-$NaV_2O_5$, the ground state becomes a singlet due to magnetic couplings between such rungs, therefore such a spin ordering has not been observed. However, $\beta$-$A_{0.33}V_2O_5$ can be a candidate because the ground state of this system is not a singlet but an antiferromagnetic (AF) state.

We performed a detailed electronic and spin structure analysis of $\beta$-$Ag_{0.33}V_2O_5$ using $^{51}$V NMR and zero-field resonance (ZFR) to demonstrate whether such a spin ordering is realized or not, as well as to offer a new point of view for the confusion concerning $\beta$-$Na_{0.33}V_2O_5$. The charge distribution among Vi sites was investigated from the field ($\boldsymbol{H}$)-swept $^{51}$V NMR using a single $0.5\times4.0\times0.5$ mm$^3$ crystal prepared by self-flux method with a Czochralski (Cz) furnace. Spin direction in the AF phase was investigated with the ZFR at 4.2 K using a powder pellet sample.

The NMR measurements on $^{51}$V ($I=7/2$) contain a set of seven signals with constant separation due to the electric field gradient (EFG). The separation is proportional to the EFG, which is proportional to the charge density of local V sites. Therefore, site assignment is possible from the NMR spectra. Figures 2(a)–2(c) show typical $\boldsymbol{H}$-swept spectra in the metallic, CO, and AF phases, respectively, with $\boldsymbol{H}$ parallel to the $b$ axis, i.e., the leg direction. The transition temperatures for the CO and AF phases are 90 and 27 K, respectively. Three sets of seven signals in Figs. 2(a) and 2(b) come from three crystallographically inequivalent sites V1, V2, and V3 as seen in Fig. 3(a). The sites were assigned from analysis of the peak separations; the sites were directly assigned from the data for the $\boldsymbol{H}$ parallel to the ac plane as mentioned below. Information of the peak separations in Fig. 2(b) appears in the fitting curves of Fig. 3(b) via asymmetric factors of the EFG.

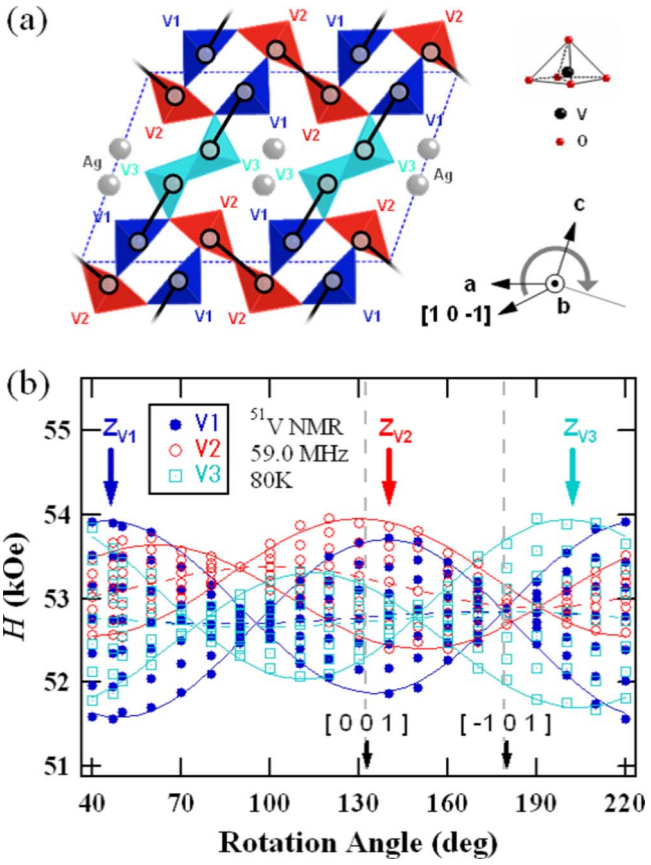


FIG. 3. (Color online) (a) Pyramid structure $ViO_5$ ($i=1$, 2, and 3) in $\beta$-$Ag_{0.33}V_2O_5$. Coupling between V1 and V3 forms two-leg ladder covalency along the $b$ axis, and coupling between two V2 forms the other one. (b) Angle dependence of $^{51}$V-NMR signals in the CO phase measured for the field $\boldsymbol{H}$ parallel to the ac plane. The angle was measured from [1, 0, −1] direction [see Fig. 3(a)]. $Z_{Vi}$ ($i=1$, 2 and 3) represent angles of the maximum splitting for each Vi site. The data for the $\boldsymbol{H}$ parallel to the $b$ axis are shown as the sharp signals in Fig. 1(b).

In the CO phase, broad basal signals emerged in addition to the sharp ones, as shown in Fig. 2(b). The uniform charge distribution breaks down because of the metal-insulator transition, causing charge disproportion within each Vi site. The sharp and broad signals are essentially of the same character as those for the metallic and AF phases, respectively. Therefore, the sharp and basal signals originate from magnetic Vi sites and nonmagnetic Vi sites, respectively. In fact, the spin-spin relaxation rate, which provides a measure of magnetic fluctuation, of the basal signals was much smaller than that for the sharp signals. The intrinsic line width of the basal signals should be much narrower than they look. The signals broaden owning to some disorders. In the AF phase, the sharp signals disappear because a large internal field caused by spin ordering shifts the resonance positions upward. The

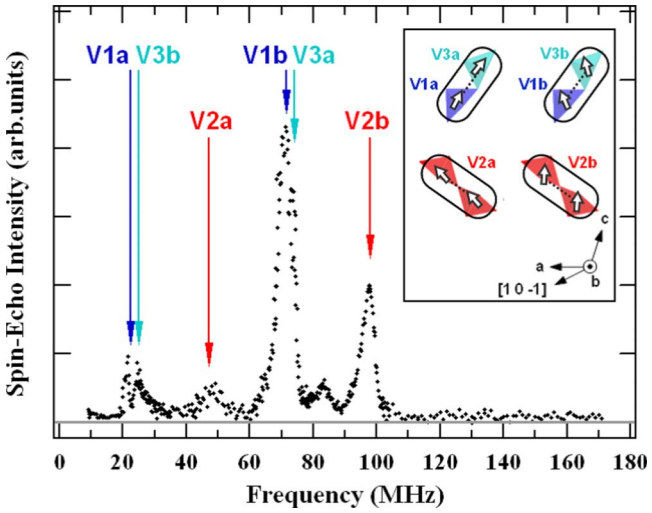


FIG. 4. (Color online) ZFR measured up to 170 MHz with a separation of 0.25 MHz/point. The arrows in the inset represent spin directions observed at nuclear sites.

signals were observed as ZFR signals. The basal signals broadened in a much wider $\boldsymbol{H}$ range in the AF phase because of dipole coupling with surrounding ordered moments.

According to the theoretical investigation, V1 and V3 chains form a ladder covalency, and two V2 chains form another one as shown in Fig. 3(a).[3] In the case that each Vi site forms a pyramid structure, the apical direction becomes an EFG-maximum direction, i.e., the first principle axis. The fact is supported by the experimental results that the maximum splitting angles of the sharp signals are consistent with the apical directions as shown in Fig. 3(b). The peak separation at the maximum splitting angles is estimated to be 0.44, 0.28, and 0.42 MHz for V1, V2, and V3, respectively. Thus, the charge distribution is almost the same for the magnetic Vi sites. Note that these values are intermediate between representative values of magnetic $V^{4+}O_5$ pyramids observed in $CaV_2O_5$ and nonmagnetic $V^{5+}O_5$ pyramids in $V_2O_5$, i.e., 0.96 and 0.07 MHz, respectively.[17] The EFG is proportional to the charge density, therefore the present results suggest formation of molecular orbitals at two V sites.

Spin alignment in the AF phase can be investigated from ZFR measurements as shown in Fig. 4. V1 and V3 sites should possess similar local environments, because they form the two-leg ladder-type covalency.[3] Therefore, it is natural to assign the origin of the peaks at 21.5, 24.8, 72.3, and 73.0 MHz to the magnetic V1-V3 rungs. Two peaks at 48.0 and 97.8 MHz are assigned to the magnetic V2-V2 rungs. The relative intensity differs between two peaks with a separation of 49 to 50 MHz. The difference does not reflect the number of magnetic V sites contributing to the peaks because the resonance condition is not the same throughout the frequency region. The origin of the remaining small peak at 83.5 MHz is not certain at present.

The peak frequency $f_{\mathrm{peak}}$ is converted to an internal field on $^{51}V$, $|\boldsymbol{H}_n|$ using the gyromagnetic ratio of $^{51}V$, $\gamma_N = 1.1193$ MHz/kOe; $|\boldsymbol{H}_n| = f_{\mathrm{peak}}/\gamma_N$. The internal field is decomposed into Fermi-contact field $\boldsymbol{H}_F$ and dipole field $\boldsymbol{H}_{\mathrm{dip}}$, $\boldsymbol{H}_n = \boldsymbol{H}_F + \boldsymbol{H}_{\mathrm{dip}}$. $|\boldsymbol{H}_n|$ is expressed using expectation value of spin at a V site, $\langle S \rangle$ and hyperfine coupling defined as a magnetic field arising from one Bore magnetron. We denote hyperfine coupling of $\boldsymbol{H}_F$ as $A_F$, and dipole coupling as $A^{\parallel}_{\mathrm{dip}}$ and $A^{\perp}_{\mathrm{dip}}$ for spin parallel and perpendicular to the EFG maximum, respectively. When the angle between the EFG maximum and spin is $\theta_n$, $|\boldsymbol{H}_n|$ is written as

$$|\boldsymbol{H}_n| = 2\langle S \rangle k \sqrt{A^{\parallel 2} \cos^2 \theta_n + A^{\perp 2} \sin^2 \theta_n}, \tag{4}$$

where $A^{\parallel(\perp)} = A_F + A^{\parallel(\perp)}_{\mathrm{dip}}$ and $k$ is a reduction factor due to the covalent effect with the O ions. We used $k = 0.8$ and $A_F = -100$ kOe as typical values. The values of $A^{\parallel}_{\mathrm{dip}}$ and $A^{\perp}_{\mathrm{dip}}$ are calculated to be $-130$ and 65 kOe, respectively, from the following equations:

$$A^{\parallel}_{\mathrm{dip}} = -\frac{4}{7}\frac{2}{\langle r^3 \rangle}\mu_B, \tag{5}$$

$$A^{\perp}_{\mathrm{dip}} = +\frac{2}{7}\frac{2}{\langle r^3 \rangle}\mu_B, \tag{6}$$

where we used the radius average of a free $V^{4+}$ ion; $\langle r^3 \rangle = 3.68$ a.u..

We mention the required conditions for $\langle S \rangle$ in Eq. (4) prior to discussing possible spin directions. When Vi is equivalent in charge distribution, as shown by the NMR results, a $3d^1$ electron should be included within three rungs stacked in the leg direction to maintain electrical neutrality. If a $3d^1$ electron is shared by $n$ sites, $\langle S \rangle$ should be

$$\langle S \rangle = 1/2n, \tag{7}$$

as is shown in Eqs. (2) and (3). Our experimental results indicate that the value of $n$ should satisfy the relation $1.5 \leq n \leq 2.1$ to cover all of the peaks observed in the ZFR. The result of $n=2$ holds for a wide range of $A_F$ ($-90 \leq A_F \leq -110$ kOe). The experimental result suggests that a $3d^1$ electron is shared within a rung and excludes the possibility of the simple CO model where a $3d^1$ electron is located on a V site.

The appearance of two sets of signals in the AF phase indicates the existence of two spin directions. The spin directions are determined from the ZFR-peak positions. The angles [$\theta_n$ in Eq. (4)], measured from the EFG-maximum direction in the ac plane, are 46, 47, 79, and 82 degrees for the two V1 and V3 sites, and 19 and 64 degrees for the two V2 sites, respectively. The spin directions observed at the nuclear sites are shown in the inset of Fig. 4. The directions are almost the same within a rung which also suggests the charge sharing of a $3d^1$ electron within a rung [see Eqs. (2) and (3)]. These magnetic rungs prefer isolated positions in the ac plane to avoid Coulomb repulsion and align with threehold periodicity in the leg direction. The reason two kinds of signals are observed for each Vi site is attributed to the crystallographical peculiarity of the system. For the V1-V3 ladders, magnetic rungs are located on two crystallographically inequivalent positions in any charge-distribution patterns which satisfies threehold periodicity in the leg direction, giving an explanation for the appearance of two signals. For the two V2s ladders, two sets of magnetic rungs are induced by local arrangement of the V1-V3 magnetic rungs,

although the two V2s rungs are crystallographically equivalent.

An important problem is why the charge sharing is observed for the vanadate spin-ladder systems. In the case that two electrons exist on a rung, the charge sharing hardly occurs because of the large Coulomb interaction. On the contrary, the $3d^1$ orbital of the vanadates can extend over several sites owning to the low electron density. As a comparable system, a spin-ladder cuprate $Sr_xCa_{14-x}Cu_{24}O_{41}$ $(0 \leq x \leq 14)$ is pointed out. There are many common features between them; the systems possess ladder planes with the trellis-lattice structure, both are pressure-induced superconductors, and so on. In the cuprate ladder system a CDW state was observed at the end material $Sr_{14}Cu_{24}O_{41}$.[18] The CDW disappears with increasing Ca substitution $(x \leq 8)$, i.e., hole doping, and superconductivity emerges at $x \geq 11.5$ by applying a pressure of over 3 GPa.[19] The valence of Cu varies from +2.1 to +2.2 with increasing Ca substitution.[20] In this system the charge sharing is not realized.

A degree of confinement depends on the Coulomb repulsions between neighboring sites. If the Coulomb repulsions are large, localization of a $3d^1$ electron on a site would occur.[14] In the present case, the weak repulsion and low electron density seem essential for the charge sharing. The ground state of $\beta$-$Ag_{0.33}V_2O_5$ is the AF state, whereas that of $\alpha$-$NaV_2O_5$ is a singlet state. The difference comes from a degree of lattice modulation and dimensionality when a magnetic rung is regarded as a unit. $\alpha$-$NaV_2O_5$ seems to possess stronger character as a one-dimensional magnetic system than $\beta$-$Ag_{0.33}V_2O_5$.

To summarize the NMR and ZFR results, the charge density of the V1-V3 and V2-V2 ladders is almost the same, and a $3d^1$ electron with $S=1/2$ is shared within a rung in both CO and AF phases. The facts were observed as a half of the electric field gradient and internal field arising from $V^{4+}$ in the CO and AF phases, respectively. The present experiment is the first observation of a spin ordering of a $3d^1$ electron shared within a rung.

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[1] T. Yamauchi, Y. Ueda, and N. Môri, Phys. Rev. Lett. **89**, 057002 (2002).
[2] T. Yamauchi, M. Isobe, and Y. Ueda, Solid State Sci. **7**, 874 (2005).
[3] M. L. Doublet and M. B. Lepetit, Phys. Rev. B **71**, 075119 (2005).
[4] Y. Ueda, J. Phys. Soc. Jpn. (Suppl. B) **69**, 149 (2000).
[5] H. Yamada and Y. Ueda, J. Phys. Soc. Jpn. **68**, 2735 (1999).
[6] Y. Ueda, H. Yamada, M. Isobe, and T. Yamauchi, J. Alloys Compd. **317-318**, 109 (2001).
[7] J. Merino and R. H. McKenzie, Phys. Rev. Lett. **87**, 237002 (2001).
[8] J. Yamaura, M. Isobe, H. Yamada, T. Yamauchi, and Y. Ueda, J. Phys. Chem. Solids **63**, 957 (2002).
[9] C. Sellier, F. Boucher, and E. Janod, Solid State Sci. **5**, 591 (2003).
[10] C. Presura, M. Popinciuc, P. H. M. van Loosdrecht, D. van der Marel, M. Mostovoy, T. Yamauchi, and Y. Ueda, Phys. Rev. Lett. **90**, 026402 (2003).
[11] M. Heinrich, H. A. Krug von Nidda, R. M. Eremina, A. Loidl, C. Helbig, G. Obermeier, and S. Horn, Phys. Rev. Lett. **93**, 116402 (2004).
[12] S. Nagai, M. Nishi, K. Kakurai, Y. Oohara, H. Yoshizawa, H. Kimura, Y. Noda, B. Grenier, T. Yamauchi, J. Yamaura, M. Isobe, Y. Ueda, and K. Hirota, J. Phys. Soc. Jpn. **74**, 1297 (2005).
[13] M. Itoh, I. Yamauchi, T. Kozuka, T. Suzuki, T. Yamauchi, J. I. Yamaura, and Y. Ueda, Phys. Rev. B **74**, 054434 (2006).
[14] H. Seo and H. Fukuyama, J. Phys. Soc. Jpn. **67**, 2602 (1998).
[15] M. Isobe and Y. Ueda, J. Phys. Soc. Jpn. **65**, 1178 (1996).
[16] T. Yamauchi, H. Ueda, J. I. Yamaura, and Y. Ueda, Phys. Rev. B **75**, 014437 (2007).
[17] H. Iwase, M. Isobe, Y. Ueda, and H. Yasuoka, J. Phys. Soc. Jpn. **65**, 2397 (1996).
[18] T. Vuletić, B. Korin-Hamzić, S. Tomić, B. Gorshunov, P. Haas, T. Rõõm, M. Dressel, J. Akimitsu, T. Sasaki, and T. Nagata, Phys. Rev. Lett. **90**, 257002 (2003).
[19] M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mori, and K. kinoshita, J. Phys. Soc. Jpn. **65**, 2764 (1996).
[20] T. Osafune, N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett. **78**, 1980 (1997).