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Coexistence of double alternating antiferromagnetic chains in $(VO)_2P_2O_7$: NMR study

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Nuclear magnetic resonance (NMR) of ^{31}P and ^{51}V nuclei has been measured in a spin-1/2 alternating-chain compound $(VO)_2P_2O_7$. By analyzing the temperature variation of the ^{31}P NMR spectra, we have found that $(VO)_2P_2O_7$ has two independent spin components with different spin-gap energies. The spin gaps are determined from the temperature dependence of the shifts at ^{31}P and ^{51}V sites to be 35 K and 68 K, which are in excellent agreement with those observed in the recent inelastic neutron scattering experiments [A.W. Garrett *et al.*, Phys. Rev. Lett. **79**, 745 (1997)]. This suggests that $(VO)_2P_2O_7$ is composed of two magnetic subsystems showing distinct magnetic excitations, which are associated with the two crystallographically inequivalent V chains running along the *b* axis. The difference of the spin-gap energies between the chains is attributed to the small differences in the V-V distances, which may result in the different exchange alternation in each magnetic chain. The exchange interactions in each alternating chain are estimated and are discussed based on the empirical relation between the exchange interaction and the interatomic distance. [S0163-1829(99)03533-X]

I. INTRODUCTION

Low-dimensional quantum-spin systems with antiferromagnetic interactions exhibit various interesting phenomena of collective nature. Vanadyl pyrophosphate $(VO)_2P_2O_7$ is a gapped antiferromagnet with spin 1/2 and had long been known as a good model compound of a two-leg antiferromagnetic Heisenberg spin ladder.[1–3] Recently, dispersion of the magnetic excitations was measured using the inelastic neutron-scattering technique and is found to be inconsistent with a simple ladder model.[4] Although an alternating Heisenberg antiferromagnetic chain is proposed as an alternative magnetic model of $(VO)_2P_2O_7$, the suggested direction of the chain is not readily known from the crystal structure and the excitation spectrum is not fully compatible with a simple alternating spin chain. It is still a controversy what magnetic model describes best the magnetic behavior of $(VO)_2P_2O_7$.

The ladder interpretation of $(VO)_2P_2O_7$ is based on the intuitive consideration of the crystal structure which is shown schematically in Fig. 1. $(VO)_2P_2O_7$ belongs to the monoclinic space group $P2_1$ and has unit-cell dimensions of $a=7.28$ Å, $b=16.59$ Å, $c=9.58$ Å, and $\beta=89.98°$ at room temperature.[5] The vanadium atoms are tetravalent to have spin-1/2 degrees of freedom, each of which is coordinated pyramidally by oxygen atoms. The VO_5 pyramids form pairs in opposite phases in the *b* direction by sharing their edges, and are stacked in pairs along the *a* axis to make up a two-leg ladder. The ladders are linked by PO_4 tetrahedra and form a three-dimensional lattice structure. The proposed direction of the alternating chain is along the *b* axis which is perpendicular to the ladder axis and the chain includes PO_4 tetrahedra as one of the important exchange pathways.[4] There are eight inequivalent V and P sites in the unit cell, so that the ladders and chains are not all crystallographically equivalent.

The magnetic susceptibility of $(VO)_2P_2O_7$ has a broad maximum around 80 K and decreases rapidly at low temperatures. Johnston *et al.*[1] have pointed out that $(VO)_2P_2O_7$ has a spin-singlet ground state owing to the ladder configuration of magnetic atoms, although the spin-1/2 alternating Heisenberg antiferromagnetic chains described by the Hamiltonian

$$\mathcal{H}=\sum_i \left(J_1\mathbf{S}_{2i}\cdot\mathbf{S}_{2i+1}+J_2\mathbf{S}_{2i+1}\cdot\mathbf{S}_{2i+2}\right) \tag{1}$$

accurately reproduces the susceptibility of $(VO)_2P_2O_7$. Numerical calculations of the susceptibility of both the two-leg ladder and the alternating chain showed that both models fit the susceptibility of $(VO)_2P_2O_7$ quite well, so that the susceptibility measurement alone cannot distinguish which model is appropriate.[2] The calculations also showed that the

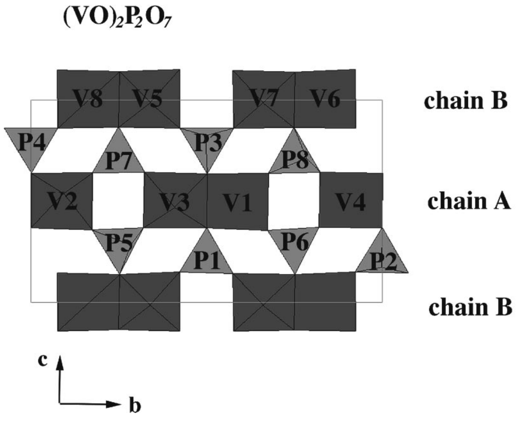

FIG. 1. Polyhedral view of the crystal structure of $(VO)_2P_2O_7$. Also indicated are site indices of the inequivalent V and P atoms included in each polyhedron. The structural units indicated are stacked in the *a* direction. See text for the labeling of the chains directed along the *b* axis.

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magnitude of the spin gap is different depending on the models, which can be tested by inelastic neutron scattering (INS) experiments. The subsequent INS measurement on powder sample of $(VO)_2P_2O_7$ has detected a spin gap of 3.7 meV, which favors the ladder model.[3]

More recently, however, Garrett *et al.*[4] have presented a surprising INS result on the magnetic excitations from an array of a lot of small single crystals. They found that the spin excitation is predominantly one dimensional but is directed along the crystalline *b* axis rather than the ladder (the crystalline *a*) axis. The exchange interaction along the *a* axis is ferromagnetic and is order of magnitude smaller than that along the *b* axis, and there is essentially no dispersion along the *c* axis. As the most likely model to account for the INS result, they proposed that $(VO)_2P_2O_7$ has alternating antiferromagnetic chains running in the *b* direction with unexpectedly strong V-V exchange via the PO_4 complexes. The exchange interaction J_1 via the PO_4 complexes is as large as 10–12 meV and the alternation ratio J_2/J_1 is estimated to be ~ 0.8. A possible importance of the superexchange pathways through the PO_4 complexes was pointed out nearly a decade ago by Beltrán-Porter *et al.* to account for the magnetic properties of various vanadyl phosphates,[6] and has recently been observed by INS in the dimer counterpart $VODPO_4 \cdot \frac{1}{2} D_2O$.[7]

Another important but unresolved finding of Garrett *et al.* is the existence of a second excitation mode whose zone-center gap is 5.7 meV. They associated it with the two-magnon bound state as it lies just below 2Δ ($\Delta = 3.1$ meV being the gap for the one-magnon excitation determined by Garrett *et al.*). However, as they have pointed out, the substantial intensity of the second mode is difficult to interpret for the two-magnon bound state. Frustrated interchain coupling has recently been suggested to give rise to a triplet two-magnon bound state just below 2Δ which is observable over a large part of the Brillouin zone.[8,9] However, the model is rather complicated and cannot reproduce correctly the intensity of the second mode especially near the zone center, where the distinct peak of the second mode is observed opposed to the theoretical prediction.

In this paper, we report on the results of ^{31}P and ^{51}V NMR on $(VO)_2P_2O_7$ powder. We have found two independent magnetic subsystems existing in $(VO)_2P_2O_7$ whose spin gaps are exactly the same as those of two distinct modes in the spin-excitation spectrum. The existence of two magnetic subsystems with different spin gaps is supported by the recent high-field magnetization measurement.[10] From crystallographic considerations and a possible correlation between the exchange interaction and the interatomic distance, we suggest that $(VO)_2P_2O_7$ has two inequivalent alternating antiferromagnetic chains directed along the *b* axis. The role of the PO_4 complexes as the exchange media and in determining the microscopic magnetic properties of $(VO)_2P_2O_7$ will also be discussed in detail.

This paper is organized as follows. We start with describing experimental details in Sec. II. The results of the NMR measurements will be presented in Sec. III. The analysis of the line shape, the shift, and the nuclear spin-lattice relaxation rates will also be given in Sec. III. Section IV is devoted to the discussion of the experimental results and their interpretations, followed by a conclusion drawn from the present experimental findings in Sec. V.

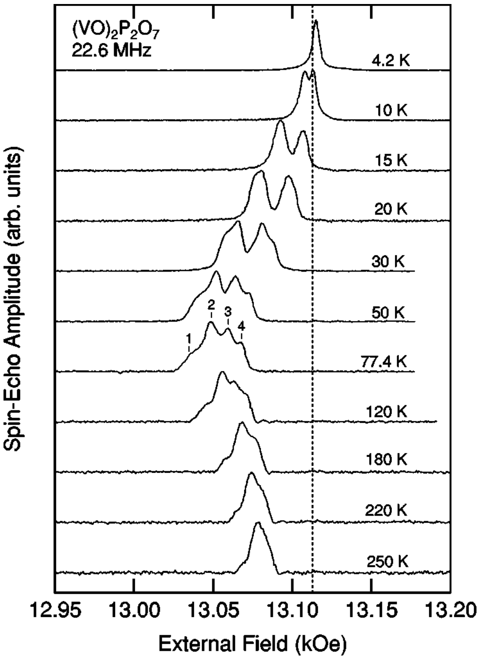

FIG. 2. Temperature variation of the ^{31}P NMR spectrum taken at 22.6 MHz. The dashed line indicates the position of the zero shift ($K = 0$) for ^{31}P nuclei calculated using the nuclear gyromagnetic ratio $^{31}\gamma_n = 17.235$ MHz/T. Numbering of the peaks (see text) is shown for the spectrum at 77.4 K.

II. EXPERIMENT

Polycrystalline sample of $(VO)_2P_2O_7$ is prepared by following several steps of reaction. The first step is to synthesize $VOPO_4 \cdot 2H_2O$ as a precursor by intercalating V_2O_5 with H_3PO_4 in ethanol at room temperature for about a month. The precursor is then heated in air at 650 °C for 2 days to remove water completely. The final product $(VO)_2P_2O_7$ is obtained by reducing oxygen from $VOPO_4$ in Ar atmosphere at 700 °C for 2 days. The x-ray diffraction pattern of the obtained sample indicates that there is no trace of impurity phases. NMR measurements were performed with a standard phase-coherent-type pulsed spectrometer. The ^{31}P NMR spectra were taken by integrating the spin-echo signal with a box-car averager while sweeping the external magnetic field at a fixed frequency. The ^{51}V NMR spectra were obtained by Fourier transforming the free-induction-decay signal after a $\pi/2$ pulse at a fixed frequency and a magnetic field. Nuclear spin-lattice relaxation rates were measured by the saturation recovery method with a single saturation rf pulse for both the ^{31}P and ^{51}V sites.

III. RESULTS AND ANALYSIS

A. ^{31}P NMR

1. Line shape and the shifts

The field-swept ^{31}P NMR spectra taken at various temperatures are shown in Fig. 2. Several peaks are found in the spectrum as expected from the crystal structure, and the line shape is strongly temperature dependent. At 4.2 K, a sharp single peak was observed near the zero shift $K = 0$, indicating the nonmagnetic ground state of $(VO)_2P_2O_7$. The width of the spectrum is very narrow (~ 4 Oe) and is attributed to

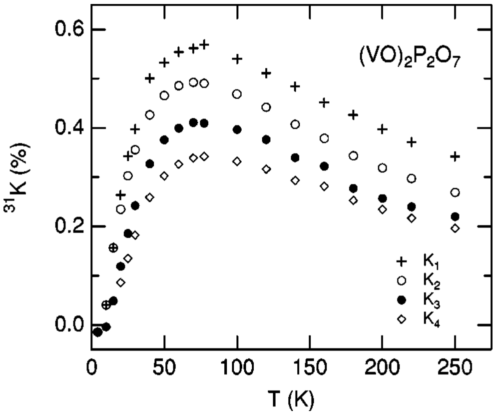

FIG. 3. Temperature dependence of the shifts at ^{31}P sites.

the broadening due to P nuclear dipoles. The absence of inhomogeneous broadening of the spectrum assures the homogeneity of the sample in a microscopic scale and the extremely low concentration of paramagnetic impurities. As the temperature increases, the spectrum splits into two peaks at first, and each peak further splits to show fine structure. Such a fine structure was not observed in the previous reports probably because of inhomogeneous broadening.[11,12] The multipeak structure can be seen most clearly around 80 K where the resonance lines are most distant from the $K=0$ position. There are four peaks visible in this temperature region, indicating that there exists at least four distinct P sites which feel different local magnetic fields from surrounding V atoms. Note that the number of the observed peaks is less than the number of the crystallographically-inequivalent P sites. This suggests that the site distinction among some P sites is not clear and is indistinguishable in the present experiment. In the following, the observed peaks are referred to as the peaks 1–4 from low-field side to the higher. As the temperature is increased further, the fine structure is obscured and the spectrum merges into a single peak again (although the structure is visible at 250 K).

The nonmonotonous variation of the line shape with temperature suggests the existence of several spin components having different spin susceptibility ($\chi_{\rm spin}$). To trace the temperature (T) dependence of each spin component, we deconvoluted the spectrum into four Gaussians and determined the shift of each peak K_i ($i=1$, 2, 3, 4). The results are shown in Fig. 3 where K_i's are plotted as a function of temperature. The T dependences of the K_i's are distinct from each other in magnitude but are similar in that they all exhibit a broad maximum around 80 K corresponding to the bulk magnetic susceptibility.[13] At low temperatures, all the K_i's decrease rapidly to almost zero owing to the gap in the spin-excitation spectrum.

The difference of the shifts at the crystallographically inequivalent nuclear sites is usually attributed to the difference of the hyperfine coupling constants if there is only one kind of spin component. However, this is not the case in (VO)$_2$P$_2$O$_7$. Figure 4(a) shows the shift of peak 3 (K_3) plotted against the shift of peak 2 (K_2) with temperature the implicit parameter. If the T dependence of K_2 and K_3 is the same, the K_3 versus K_2 plot should lie on a straight line and its slope gives the ratio of the coupling constants A_3/A_2 (A_i being the hyperfine coupling constant at P sites associated with the peak i). It is obvious from Fig. 4(a) that K_3 does not scale to K_2 at low temperatures (near the origin of the K_3-K_2 plot). There the K_3 versus K_2 plot is concave downward, which indicates that K_2 increases more rapidly with increasing temperature than K_3. This suggests that there are at least two independent spin components in (VO)$_2$P$_2$O$_7$ whose $\chi_{\rm spin}$'s are mutually different.

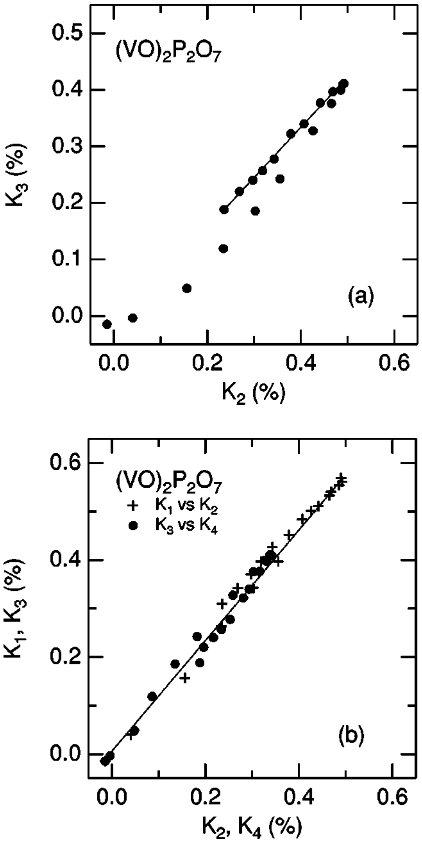

FIG. 4. (a) The shift of the peak 3 (K_3) plotted against the shift of the peak 2 (K_2) with temperature the implicit parameter. The straight line is a fit of the data from 100 to 250 K. (b) Plots of K_1 vs K_2 and K_3 vs K_4. The line is a guide to the eyes of which slope corresponding to the average of A_1/A_2 and A_3/A_4.

It is interesting to note that at relatively high temperatures, a nice linear relation is found between K_3 and K_2. This indicates that the T dependence of $\chi_{\rm spin}$'s responsible for K_3 and K_2 is almost identical in this temperature region. This is not surprising because at temperatures much higher than the exchange interactions, spins behave paramagnetically and the asymptotic relation $\chi_{\rm spin}\approx C/T$ with C the Curie constant for $S=1/2$ is expected to hold for all the spin components. From the slope of this linear portion, the ratio of the hyperfine coupling constants A_3/A_2 is determined to be 0.88 ± 0.02.

We have made a similar analysis for all possible pairs of K_i's and have found that the observed four peaks can be divided into two groups. These are peaks 1 and 2 (group I) and peaks 3 and 4 (group II), each of which shows distinct T dependence of the shifts. This indicates that there exist two independent spin components in (VO)$_2$P$_2$O$_7$. Figure 4(b) shows the plots of K_1 versus K_2 and K_3 versus K_4 similar to Fig. 4(a). A linear relation is found between K_1 (K_3) and K_2 (K_4), indicating that their T dependences are identical

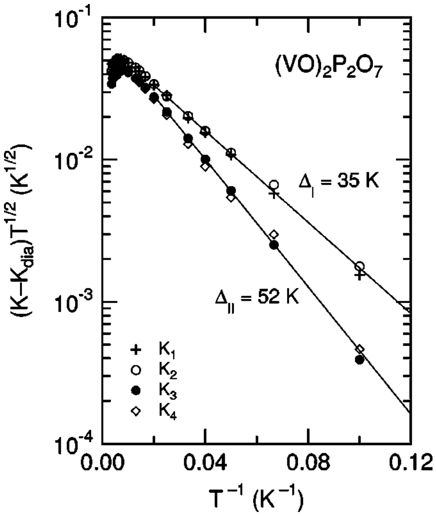

FIG. 5. Plots of $(K-K_{\mathrm{dia}})T^{1/2}$ against $1/T$. The data for K_1 and K_4 are plotted by multiplying the scaling factors A_2/A_1 and A_4/A_3 to absorb the difference of the hyperfine coupling constants within the groups. The lines indicate the activation law $(K-K_{\mathrm{dia}})T^{1/2} \propto \exp(-\Delta/T)$ with Δ of 35 K and 52 K for groups I and II, respectively. The Δ's were determined from the least-square fit of the data below $T \leqslant 25$ K (see text).

aside from the T-independent prefactors (or A_i's). It is surprising that both plots lie on almost the same straight line in spite of the difference in the T dependence between the groups. Indeed, the ratios of the coupling constants $A_1/A_2 = 1.15 \pm 0.03$ and $A_3/A_4 = 1.18 \pm 0.04$ agree within experimental accuracies. This suggests that both P groups have a similar local environment with regard to the site distinction among P sites within the same group. It is also noted that the intensity ratio of the two different P groups is close to unity $(I_{\mathrm{I}}/I_{\mathrm{II}} = 1.1 \pm 0.1)$. This indicates that the number of nuclei contributing to the NMR line of each P group is almost the same.

As demonstrated in Fig. 4(a), the difference in the T dependence of the shifts at P sites belonging to the different groups is evident at low temperatures. This implies that the magnitude of the spin gap is different for the individual spin components. To estimate the gap of each spin component, we analyzed the K_i's based on the susceptibility of a gapped one-dimensional spin system.[14,15] If the magnon dispersion along the chain is approximated by the quadratic form $\epsilon(k) \simeq \Delta + c^2k^2/2\Delta$ near the bottom of the dispersion $(k = q - \pi \sim 0)$, the T dependence of the susceptibility χ in the low-temperature limit $T \ll \Delta$ is expressed as

$$\chi = \sqrt{\frac{2\Delta}{\pi c^2 T}} e^{-\Delta/T} \tag{2}$$

where c is the spin velocity. We fitted the K_2 (group I) and K_3 (group II) data below 25 K to the form $K = K_{\mathrm{dia}} + \alpha T^{-1/2} \exp(-\Delta/T)$ where K_{dia} is a T-independent diamagnetic contribution to the shifts. The obtained values are $K_{\mathrm{dia}} = -0.016 \pm 0.005\,\%$ for both K_2 and K_3, $\alpha = 0.065 \pm 0.002$ $\mathrm{K}^{1/2}$ and $\Delta = 35 \pm 2$ K for K_2, and $\alpha = 0.079 \pm 0.002$ $\mathrm{K}^{1/2}$ and $\Delta = 52 \pm 3$ K for K_3. The results of the fit are shown in Fig. 5 where we plotted $(K-K_{\mathrm{dia}})T^{1/2}$ against $1/T$. We also plotted in the same figure the corresponding values of K_1 and K_4 with the appropriate scaling factors (i.e. the ratios A_1/A_2 and A_3/A_4 determined above) and K_{dia}. The correspondence between K_1 (K_3) and K_2 (K_4) is quite good. It should be noted that the estimated gap $\Delta_{\mathrm{I}} = 35$ K for the group I agrees within the experimental accuracy with the gap of the lower mode (36 K) observed in the INS on single crystals, while the gap $\Delta_{\mathrm{II}} = 52$ K for the group II is somewhat smaller than the gap for the upper mode (67 K).

The observed two independent spin components in $(VO)_2P_2O_7$ may be associated with the two crystallographically inequivalent magnetic chains running along the b axis. The two chains have different alternation in the V-V distances, so that the gap may be different from each other. This would give a natural explanation for the existence of the second mode in the excitation spectrum; i.e., the second mode is not the two-magnon bound state but the independent magnetic excitation from another alternating antiferromagnetic chain with a larger spin gap. The fact that the NMR lines for the groups I and II have almost the same intensity supports this interpretation.

If we assume that the T dependence of χ_{spin}'s of the two spin components is identical at high temperatures which is justified by the presence of a linear region in the K_3 versus K_2 plot, the absolute values of the A_i's can be estimated from the slopes of the usual K-χ plots. The plots of the K_i's against χ all have linear regions at high temperatures, the slopes of which yield $A_1 = 20 \pm 2$ kOe/μ_{B}, $A_2 = 17 \pm 1$ kOe/μ_{B}, $A_3 = 15 \pm 1$ kOe/μ_{B}, and $A_4 = 13 \pm 1$ kOe/μ_{B}. These values give the ratios A_3/A_2, A_1/A_2, and A_3/A_4 consistent with those determined independently from the K-K scaling shown in Fig. 4.

2. Nuclear spin-lattice relaxation rates

The existence of two independent spin components with different energy gaps in $(VO)_2P_2O_7$ will be demonstrated more directly if the nuclear spin-lattice relaxation rates $1/T_1$ for the different P groups can be measured separately. However, the peaks overlap severely in the spectrum over a wide temperature range, which makes independent determination of $1/T_1$ rather difficult. We therefore measured $1/T_1$ in the limited temperature range from 12.5 to 30 K where the peaks for the different P groups are well articulated, and have successfully determined $1/T_1$ for groups I and II.

The recovery curves were taken at the peak position of each resonance line. To avoid excitations of nuclear spins belonging to the different group, we used a relatively small rf exciting field H_1. A typical strength of H_1 was 14 Oe which exceeds the width of each peak and is still smaller than the line splitting (25–30 Oe at 31.4 MHz where the measurements were performed). The recovery curves can be fitted to an exponential function as illustrated in Fig. 6, indicating that we reliably separate the signal from the different P group.

The T dependences of $1/T_1$ are shown in Fig. 7. It is clear that the $1/T_1$ for the different P groups show an activated behavior with different activation energies. By fitting the data to an activation form $1/T_1 \propto \exp(-\Delta'/T)$, we obtained the gaps $\Delta'_{\mathrm{I}} = 53$ K and $\Delta'_{\mathrm{II}} = 71$ K for groups I and II, respectively. The gap is larger for group II which is consistent with the shift measurement. It is also noted that the ratio of

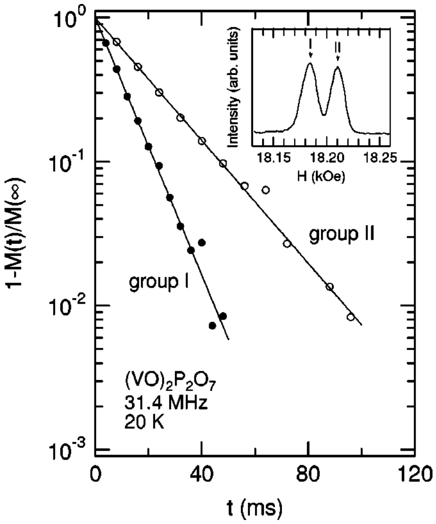

FIG. 6. Typical examples of the recovery curve of ^{31}P nuclear magnetization. The data were taken at 31.4 MHz and 20 K. The inset shows the field-swept ^{31}P NMR spectrum at the same frequency and temperature. Arrows in the inset indicate the positions of the external fields where the recovery curves are measured.

the two gap energies $\Delta'_{\mathrm{II}}/\Delta'_{\mathrm{I}}=1.34\pm0.10$ for $1/T_1$ agrees roughly with that of the shifts $\Delta_{\mathrm{II}}/\Delta_{\mathrm{I}}=1.48\pm0.10$. However, the absolute values of the gap determined from $1/T_1$ are larger than those obtained from the shifts as has been observed in other gapped quantum-spin systems. [16–18]

B. ^{51}V NMR

The results of the ^{31}P NMR experiments show that $(VO)_2P_2O_7$ has two independent spin components with different energy gaps for the spin excitations. This accounts for quite naturally the existence of two distinct excitation modes which are likely to come from the two inequivalent V chains running along the b axis. However, one of the gap energies estimated from the shift does not agree with the one observed in the INS (Ref. 4) and magnetization measurements[10] that needs further examinations. This is partly because P nuclei feel transferred hyperfine fields from both spin components, which may result in the ambiguity in the estimation of the gap energy. The ^{51}V NMR is free from such an ambiguity because of a dominant on-site hyperfine coupling and is expected to give a more precise measure of the T dependence of χ_{spin} of each spin component.

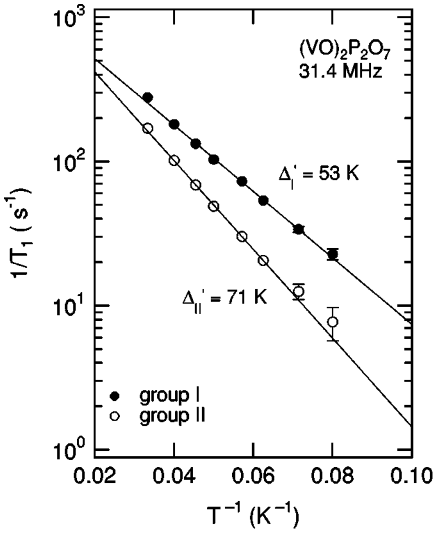

FIG. 7. Temperature dependences of $1/T_1$ at the ^{31}P sites belonging to groups I and II. Solid lines are the results of the least-squares fit of the data to the activation law $1/T_1\propto\exp(-\Delta'/T)$ with Δ' of 53 K and 71 K for groups I and II, respectively.

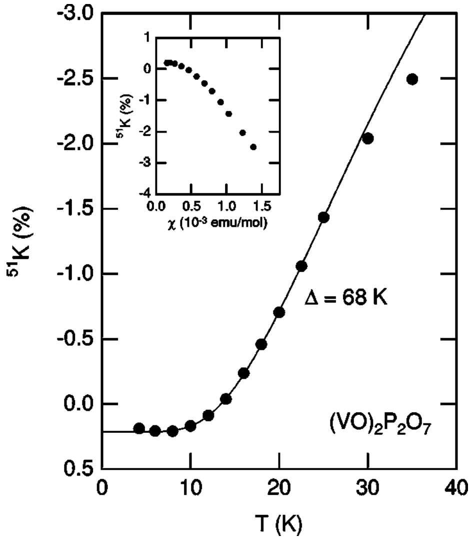

FIG. 8. Temperature dependence of the shift ^{51}K at the ^{51}V sites. The solid line is a fit of the data with a gap of 68 K (see text). The inset shows ^{51}K plotted against the bulk magnetic susceptibility.

An intense free-induction-decay (FID) signal from V nuclei has been observed at low temperatures. The frequency spectrum obtained from the Fourier transform of the FID signal is isotropic with a full width at half maximum (FWHM) of about 70 kHz at 15.8 MHz and 4.2 K.[19] The FWHM is nearly T independent and there is no indication of the line splitting up to 35 K. We could not trace the signal above 35 K due both to the poor signal-to-noise ratio and to the shortening of the nuclear-spin relaxation time which prevents us from observing any transient signals by a pulsed NMR technique.

Figure 8 shows the T dependence of the shift ^{51}K at the peak position of the spectrum. The shift is nearly constant below 10 K and varies strongly with temperature above 10 K. In general, the shift K of a nucleus belonging to the magnetic atom can be written as the sum of spin and orbital contributions, $K=K_{\mathrm{spin}}+K_{\mathrm{orb}}$. By assuming that χ_{spin} vanishes at $T=0$ owing to the spin gap, the orbital shift K_{orb} at V sites is estimated to be $0.212\pm0.005\,\%$. This is comparable with $K_{\mathrm{orb}}=0.236\pm0.005\,\%$ in the reference material $VOHPO_4\cdot\frac{1}{2}H_2O$ with a similar local environment around V atoms.[20] The T dependence of K_{spin} $(=K-K_{\mathrm{orb}})$ is consistent with that of χ given in Eq. (2), and the energy gap for the V sites is determined to be 68 ± 2 K by fitting K_{spin} to be proportional to χ in Eq. (2). This value is in excellent agreement with the gap of the second mode observed in the INS experiments. The observation of the gap of the second mode via NMR suggests that the second mode is not a branch for the two-magnon bound states but is simply a one-magnon propagating mode.

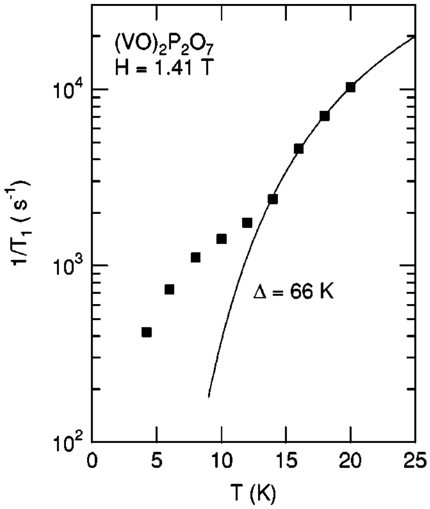

FIG. 9. Temperature dependence of $1/T_1$ at the ^{51}V sites. The solid line represents the activated temperature dependence with a gap of 66 K.

The inset of Fig. 8 is a plot of ^{51}K versus bulk χ with temperature the implicit parameter. It is obvious from the figure that the ^{51}K does not scale to the bulk χ. The ^{51}K-χ plot is convex upward, which indicates that χ_{spin} responsible for the observed ^{51}K decreases more rapidly with decreasing temperature than the bulk χ. The result of the ^{51}K-χ plot also suggests that the bulk χ includes an additional contribution from the spin component with a gap smaller than that observed via ^{51}V NMR. Unfortunately, we could not detect a transient V signal corresponding to the spin component with a smaller gap energy, which results probably from the short nuclear spin-spin relaxation time T_2 of such V sites.

The T dependence of $1/T_1$ measured for the observed FID signal is shown in Fig. 9. The recovery of ^{51}V nuclear magnetization is exponential in all the temperature region and an activated behavior with a gap of 66 ± 2 K has been observed down to 14 K. Below 14 K, however, the $1/T_1$ starts to deviate from the activation law. It is probable that the deviation comes from extra relaxation processes due to impurity and/or defect spins,[21] although the origin of the exponential recovery in this temperature region is unknown. The obtained gap for $1/T_1$ agrees quite well with that determined from the ^{51}K measurement, which is expected in the low-T limit.[22] This is contrasted with the result at P sites where the gap energies for the shifts and $1/T_1$'s are different. The reason for this difference between V and P sites is not clear, although the different wave-vector dependence of the hyperfine form factor is likely to be the case.

IV. DISCUSSION

It is now evident from our NMR experiments that $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ is composed of two independent magnetic subsystems with different spin-gap energies. Since the different magnetic properties of the system generally come from the different crystallographic environment, it is reasonable to associate them with the two crystallographically inequivalent V chains running along the b axis which $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ inherently possesses. The two-chain model gives consistent explanations for most of the present experimental results such as the observation of two distinct spin gaps (and χ_{spin}'s), the intensity ratio of the resonance lines for the two different P groups, and the underestimation of one of the spin-gap energies. This model also accounts for the existence of the two distinct magnetic modes, which have been thought to be a one-magnon and the two-magnon bound states of the same alternating antiferromagnetic chain.

A. Qualitative aspects

Before discussing the experimental results in detail, let us review the crystal structure of $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$. As has been noted previously, $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ has eight inequivalent V and P sites, and 36 oxygen sites in the unit cell. This makes a crystallographic difference between the two kinds of V chains running along the b axis. Chain ''A'' consists of V atoms on V1-V4 sites and chain ''B'' includes V5-V8 sites as shown in Fig. 1.[23] The V-V distances d_{VV}'s in both chains A and B alternate to give rise to the alternations of the exchange interactions, but the alternations in d_{VV}'s are slightly different between the two chains.

The difference of the spin gap and the resultant difference of χ_{spin} between the chains can be understood qualitatively by considering that the different alternations in d_{VV} results in the different alternations in the exchange interaction as well. This is very likely because the exchange interaction is expected to depend sensitively on the interatomic distance through the overlap of the related electronic orbitals. In the alternating antiferromagnetic chains, the shape of the χ-T curve varies strongly with the ratio $\alpha=J_2/J_1$.[24] Therefore, if chains A and B have different values of α owing to the different alternations in d_{VV}, they exhibit different T dependence of χ_{spin}'s. The difference of the spin gap can also be explained because the spin gap of the alternating chain depends on the ratio α as well as the magnitude of J_1 and J_2.

We did not mention explicitly the exchange pathways in the above argument. Garrett *et al.* have pointed out that the exchange via the PO_4 complexes in the b direction is essential in determining the magnetic properties of $(\mathrm{VO})_2\mathrm{P}_2\mathrm{O}_7$ as alternating antiferromagnetic chains.[4] Most of the present experimental results are consistent with such exchange pathways and are compatible with the two-chain model as described below.

For the magnetic connection along the b axis, two PO_4 complexes in between the VO_5 pyramids should be the important exchange pathways. In chain A, the exchange between V1 and V4 (V2 and V3) sites is mediated by the PO_4 complexes containing P6 and P8 (P5 and P7) sites. It includes the distant V-O-P-O-V paths. There is also the exchange coupling between V4 and V2 (V3 and V1) sites via the shared VO_5 pyramidal edge having shorter V-O-V paths. This is illustrated in Fig. 10 together with the exchange paths for chain B. As a natural consequence of the exchange via PO_4 along the b axis, eight inequivalent P sites are divided into two groups depending on to which chain they belong as the exchange paths: P5–P8 sites belonging to chain A and P1–P4 sites belonging to chain B. This is consistent with the observation of two different P groups via ^{31}P NMR. In addition, since the number of the sites is same for both P

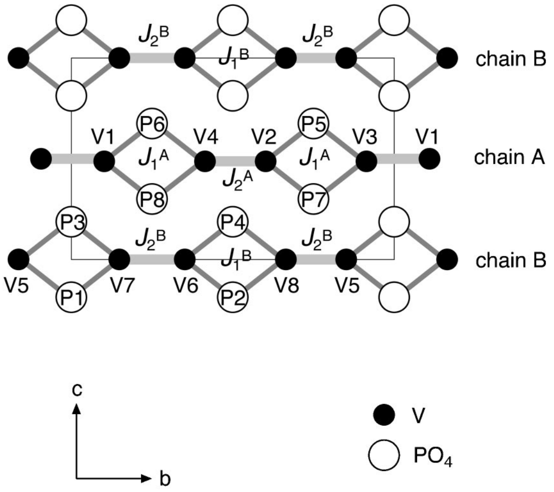

FIG. 10. Schematic description of the exchange interactions in $(VO)_2P_2O_7$. The assignment of the inequivalent P sites to each alternating chain is also shown.

groups in this model, the intensity of the NMR lines should be the same. This is what was observed in the ^{31}P NMR experiments.

The exchange coupling via the PO_4 complexes explains why the susceptibility of each spin component can be traced selectively by means of the ^{31}P NMR. In the two-chain model, the shift K_A at P sites in chain A can be written as $K_A = a_{AA}\chi_{spin}^A + a_{AB}\chi_{spin}^B$. Here χ_{spin}^A and χ_{spin}^B the spin susceptibilities of chains A and B; a_{AA} and a_{AB} are the coupling constants at P sites in chain A for the hyperfine fields transferred from the V sites in chains A and B, respectively. Similarly, for P sites in chain B, the shift K_B can be written as $K_B = a_{BA}\chi_{spin}^A + a_{BB}\chi_{spin}^B$ with a_{BA} and a_{BB} defined in a manner similar to a_{AA} and a_{AB}. Since the transferred hyperfine field at nuclear sites in between the exchange-coupled magnetic atoms arises from the electron-spin transfer similar to that for the exchange, the hyperfine field at the P site is expected to come mainly from the V atoms in the same chain. This means that $|a_{AB}|$ and $|a_{BA}|$ are much smaller than $|a_{AA}|$ and $|a_{BB}|$, indicating K_A and K_B to be roughly proportional to χ_{spin}^A and χ_{spin}^B, respectively.

It is expected that the interchain exchange coupling in the *c* direction is weakened by the presence of the intrachain coupling via the PO_4 complexes. This is because molecular orbitals of the PO_4 complex should be configured to connect the neighboring V atoms in the *b* direction, which may be a microscopic origin of the dominant hyperfine coupling between the P nucleus and the V moments in the same chain. As expected, the magnetic-excitation spectrum of $(VO)_2P_2O_7$ exhibits a very weak dispersion in the *c* direction.[4] We notice here that the weak ferromagnetic coupling in the *a* direction acts between the same kind of chain so that chains A and B are magnetically decoupled. It is to be emphasized that the periodicity of the lattice is unchanged by the resultant grouping of V and P atoms: the magnetic unit cell is identical with the chemical one for both magnetic chains. Therefore, the spin-wave dispersion is observed in exactly the same Brillouin zone. This is consistent with the INS results.

Although the contribution from the different kind of chain to the hyperfine fields at P sites is considered to be small, it affects the estimation of the gap energies from K_A and K_B. This is serious for the P group belonging to the chain with a larger spin gap for the following reason. Suppose that the spin gap Δ_B of chain B is smaller than the spin gap Δ_A of chain A. Then χ_{spin}^B starts to grow at lower temperatures than χ_{spin}^A and there may be a temperature region in which χ_{spin}^B grows rapidly with increasing temperatures while χ_{spin}^A is still vanishingly small. In such a temperature region, K_B may be approximated by $a_{BB}\chi_{spin}^B$ because both a_{AB} and χ_{spin}^A are small. Hence the value of Δ_B will be estimated correctly from K_B. On the other hand, for P sites in chain A, the contribution from the different kind of chain $a_{AB}\chi_{spin}^B$ may be comparable with, or greater than that from the same chain $a_{AA}\chi_{spin}^A$. As a result, K_A would start to increase at lower temperatures than χ_{spin}^A. This is inevitable as far as a_{AB} is finite and $\Delta_A > \Delta_B$, and will result in the underestimation of Δ_A.[25] In the present NMR experiment at P sites, the gap Δ_{II} of group II is smaller than the gap of the upper mode in the excitation spectrum, while Δ_I agrees well with the gap of the lower mode. In the light of the above argument, the underestimation of Δ_{II} is considered to result from the small but finite contribution from V sites in the different kind of chain with a smaller gap. At this point, we may associate the P sites belonging to group II (I) with the chain having a larger (smaller) spin gap. The value of the gap determined from the ^{51}V NMR experiment agrees well with the INS result and is considered to be more accurate for the larger spin-gap energy.

B. Quantitative aspects

Most of the present experimental results can be explained qualitatively in terms of the two-chain model by taking account of the relatively strong V-V exchange via PO_4 in the *b* direction. The model is consistent also with the INS result and therefore seems to be appropriate for the description of the magnetic behavior of $(VO)_2P_2O_7$. However, one crucial question arises here whether the small differences in d_{VV} can make the spin gaps of the two alternating chains be different by a factor of nearly 2. To answer this question, we estimated the exchange interactions in each alternating chain. It is found that the difference of the exchange is not very large and may be accounted for by the strong dependence of the exchange interaction on the interatomic distance.[26–29]

For the analysis, we take the values of the spin gap to be 35 K and 68 K. The former is the one determined from the shift at P sites belonging to group I, and the latter from the shift at V sites. Both are in excellent agreement with the zone-center gaps for the lower and upper modes in the spin-excitation spectrum, respectively. The zone-boundary energy ϵ_{ZB} taken from the spin-wave dispersion along the *b* axis is 15.4 meV (≈ 179 K) and is assumed to be the same for both chains.[4] Then $J = (J_1 + J_2)/2$ is calculated from the relation $\pi J/2 = \epsilon_{ZB}$ to give the ratio Δ/J, and the alternation parameter $\delta = (1-\alpha)/(1+\alpha)$ is determined by using the δ dependence of Δ/J presented by Uhrig and Schluz.[30] From the values of J and δ, the exchange interactions J_1 and J_2 are calculated. The results are summarized in Table I.

TABLE I. Spin gaps and exchange interactions in $(VO)_2P_2O_7$.

	Δ (K)	J_1 (K)	J_2 (K)	J_2/J_1
Chain A	68	136	92	0.67
Chain B	35	124	103	0.83

We have assigned chain A to have a larger exchange alternation (i.e., a larger value of δ), resulting in a larger spin gap. This is based on the following two assumptions: (1) the exchange via the PO_4 complexes is stronger than that through the shared VO_5 pyramidal edge, and (2) the interaction is weaker for longer d_{VV} for both the exchange paths. The V-V distance via the PO_4 complexes in chain A is ~ 5.14 Å, which is shorter than that in chain B of ~ 5.16 Å.[31] The largest exchange coupling ($J_1 = 136$ K) is therefore assigned to the V-O-P-O-V paths in chain A. The V-O-V path in chain A is then assigned automatically to have the smallest coupling constant ($J_2 = 92$ K) without any additional assumptions. The V-V distance is ~ 0.02 Å longer than the corresponding d_{VV} in chain B of ~ 3.21 Å and hence the assignment is self-consistent. Even if we regard the shared pyramidal edge as a dominant exchange pathway, the assignment can be made in the same way without inconsistency and now the spin gap of chain A should be smaller than that of chain B.

It appeared that the exchange interactions of chain A should differ from those of chain B by ~ 10 K ($\sim 10\%$ in relative strengths) to give rise to the observed difference of the spin gap between the two chains. Since the two-chain model is based on the crystallographic inequivalence of the chains, the difference of the exchange should be ascribed to the small differences (~ 0.02 Å for both the exchange paths) in d_{VV}. With regard to the V-V exchange via the shared pyramidal edge, the difference may be attainable because in some copper salts with edge-sharing Cu-O bondings, the 0.02 Å difference in the Cu-Cu distance gives rise to the difference in the exchange by ~ 100 K.[26] The strong dependence of the exchange on the interatomic distance is also known empirically,[27–29] putting the basis on the dependence of overlap integrals on distance. For V-V pairs sharing common pyramidal edge, the empirical law predicts the exchange to decrease with increasing d_{VV} as $(d_{VV})^{-10}$.[29] The application to $(VO)_2P_2O_7$ yields $\sim 6\%$ decrease of the V-V exchange on increasing d_{VV} from 3.21 to 3.23 Å, which is comparable with the above estimation. Although such an empirical relation is not known for V-V pairs connected by the PO_4 complexes because of the complicated and unresolved interaction pathways, it is plausible that the exchange is also sensitive to d_{VV} as the exchange via the common VO_5 edge. The small difference in d_{VV}'s between the two crystallographically inequivalent chains is therefore considered to be crucial in making them magnetically distinct from each other. Quantum chemical calculation of the exchange interaction via the PO_4 complexes is desirable for a more thorough understanding of the magnetic properties of $(VO)_2P_2O_7$.

V. CONCLUSION

We have presented the results of the extensive NMR study on the quasi-one-dimensional gapped quantum antiferromagnet $(VO)_2P_2O_7$. As revealed by the detailed line-shape analysis of the ^{31}P NMR spectra and the measurement of $1/T_1$ at ^{31}P sites, $(VO)_2P_2O_7$ has two independent spin components with different gap energies for the spin excitations. The gap energies are determined from the temperature dependence of the shifts at ^{31}P and ^{51}V sites to be 35 K and 68 K, and are found to coincide with those observed in the INS experiments.

The agreement of the gap energies between NMR and INS experiments suggests that the two magnetic modes in the excitation spectrum arise from the two distinct magnetic subsystems which $(VO)_2P_2O_7$ inherently possesses. We proposed that two crystallographically inequivalent V chains running along the *b* axis are magnetically distinct to contribute independently to the spin-excitation spectrum. The two chains have different exchange alternations and spin gaps, which may result from the small difference in the V-V distances between the chains. It is also suggested that the PO_4 complexes act as the important superexchange pathways. This is essential in dividing the P sites into two groups and in observing the susceptibility of each alternating chain selectively via ^{31}P NMR. Quantitative estimates of the exchange interactions show that the difference of the exchange is not very large and may be attributed to the difference in the V-V distances between the two chains.

To conclude, $(VO)_2P_2O_7$ is a complicated magnetic system containing two kinds of antiferromagnetic linear chains with different alternations in the exchange interaction. The energy for the spin excitations is different in each alternating chain, which is the origin of the two distinct magnetic modes in the excitation spectrum.

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