Two Gaps in $(VO)_2P_2O_7$: Observation Using High-Field Magnetization and NMR

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The alternating one-dimensional Heisenberg $S = 1/2$ chain compound with spin gap, $(VO)_2P_2O_7$, has been studied by the high-field magnetization and ^{31}P NMR measurements. Two critical phenomena at 25 ± 1 and 46 ± 2 T are observed in the magnetization curve, which are considered to be a crossover between the ground state and the excited state in two kinds of gap systems. ^{31}P NMR also revealed the coexistence of two magnetic systems with independent spin gaps. Results obtained from the present and previous studies are well explained by the model in which two kinds of magnetic chains along the b axis behave as alternating spin chains with independent gap energies.

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Since Johnston *et al.* proposed a possibility of an alternating spin chain system or a spin ladder system along the a axis from the susceptibility measurement [1] in 1987, the compound $(VO)_2P_2O_7$ has attracted much concern from a point of view of the low-dimensional $S = 1/2$ Heisenberg spin-gap system. The energy gap 3.7 meV (43 K) in magnetic excitations was directly observed in the inelastic neutron scattering experiments with a powder sample [2]. A NMR study revealed the one-dimensional character of the magnetic excitation and a spin singlet as the ground state [3]. However, it remained unsolved whether the system was a spin ladder or an alternating spin chain, and this compound was regarded as a spin ladder system from its crystal structure rather than an alternating spin chain.

In 1997, Garrett *et al.* reported results of magnetic excitations in inelastic neutron scattering experiments using an array of single crystals and concluded that the spin system is an alternating spin chain with the spin-gap energy of more precisely 3.1 meV (36 K) not along the a axis (ladder leg direction) but along the b axis [4]. Furthermore this neutron study has raised a new question as to what is the origin of the higher magnetic excitation observed at $E = 5.7$ meV (zone center) in addition to 3.1 meV. In the ESR measurement, this upper excitation (67 K) has been also observed [5]. We will discuss this question later.

The fact that the spin system is an alternating spin chain along the b axis suggests a significant superexchange interaction via the PO_4 tetrahedron. The crystal structure of $(VO)_2P_2O_7$ is schematically shown in Fig. 1 where the schematic magnetic chain system proposed in the present study is also shown. This compound has eight crystallographically different sites for both vanadium and phosphorus atoms [6]. The site indices of vanadium and phosphorus atoms, Vn (n = 1 ~ 8) and Pn (n = 1 ~ 8), are pursuant to Ref. [6]. There exist two kinds of alternating chains along the b axis in the structure. Both chains consist of edge-shared VO_5 square pyramids bridged by PO_4 tetrahedra. One chain named "chain A" contains vanadium V1 ~ V4 and phosphorus P5 ~ P8 (as superexchange paths) and the other chain named "chain B" contains vanadium V5 ~ V8 and phosphorous P1 ~ P4.

Chains A and B were regarded as identical magnetic systems in all previous studies. In this study we have obtained several new results which provide evidence for the coexistence of two different energy gaps 35 and 64 K. We show that every experimental result obtained so far in $(VO)_2P_2O_7$ can be consistently explained by assuming the coexistence of the two different magnetic chains with independent energy gaps. We will call this "the double gap model."

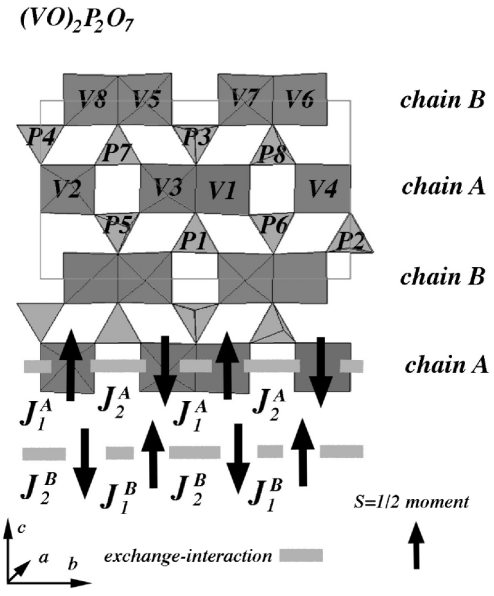

FIG. 1. The crystal structure of $(VO)_2P_2O_7$. There exist two kinds of alternating spin chains along the b axis, chains A and B, in the structure. Both chains consist of the edge-shared VO_5 square pyramids bridged by PO_4 tetrahedra. The schematic view of the magnetic interaction in both chains is also shown.

The magnetic excitations of chains A and B are visible in the inelastic neutron scattering experiments because of the same translation symmetry of both chains. Consequently the unidentified 5.7 meV (66 K) excitation in the inelastic neutron scattering experiments can be considered as the observation of the excitation in the chain with the higher energy gap.

A coexistence of multikinds of magnetic systems in one compound has been found out from several compounds. In these cases, the magnetic systems were separated from each other by large alkali/alkaline earth ions and these systems have a definitely different local environment in a crystal structure. For instance, $Sr_{14}Cu_{24}O_{41}$ has been well known as the case [7]. In contrast to this, our reported compound has a noteworthy dimension that two different but similar magnetic systems coexist at a very close distance. This distance is only as long as a main exchange path intrachain. Furthermore these two kinds of chains are connected to each other by almost same chemical bonds with intrachains. This study is the first experimental evidence of a coexistence of different ground states in a quite near distance and in quite similar spin chains. This study shall be one typical gauge of unusual low-dimensional compounds.

One of the biggest issues of modern physics is unusual behaviors of electron systems near the quantum critical point, such as the Mott transition. Recent studies on the highly correlated electron system have focused on this. These compounds β-$A_xV_2O_5$ (A = Cu, Na, Sr, etc.) and α-AV_2O_5 (A = Li, Na, ...) have several crystallographically inequivalent vanadium chains and mixed valence. Some compounds have good electrical conductivity. In a sense of electron conductivity, these compounds have been thought to be near the critical point. Some of these compounds show uniform electron state in spite of multikinds of vanadium chains and semiconductive behavior [8]. The behavior is very unusual and in good contrast with this work.

Powder samples of $(VO)_2P_2O_7$ were prepared by a combination of aqueous and solid state reactions. The details will be presented elsewhere [9]. The sample was identified to be monophase by powder x-ray diffraction measurements and the structure was characterized by the Rietveld analysis in a wide temperature region (R.T. $\sim$ 8 K). The magnetic susceptibility was measured using a Quantum Design Co. Ltd MPMS-5s SQUID system from $T = 1.7$ to 320 K between $H = 0.1$ T and 5 T. The ESR spectra were observed in X-band $\nu = 9$ GHz with an MnO marker at room temperature. The high-field magnetization measurements were performed using a pulsed high magnetic field (pulse duration time about 7 msec) up to 65 T and down to 1.3 K at KYOKUGEN in Osaka University. The NMR experiments were carried out with a standard phase-coherent-type pulsed spectrometer.

The results of the magnetization measurements in a pulsed high field are shown in Fig. 2. Two obvious inflections have been observed in the magnetization curve at the lowest temperature. The magnetization curve shows the increases of the slope around two different fields as if two independent gap systems coexist in this compound, as schematically shown in the inset of Fig. 2.

The lower critical field H_{c1} and the higher one H_{c2} are estimated to be 25 $\pm$ 1 T and 46 $\pm$ 2 T, respectively, from the extrapolation shown in the magnetization curve at the lowest temperature. Since a small magnetization in the lower field region ($H < H_{c1}$) was thought to be due to spins associated with crystallographic planar faults [9], it was omitted from the discussion in the present study.

Such an increase of magnetization in two steps is the first observation and is never expected in simple spin-gap systems like spin ladders, alternating spin chains, etc. The two-magnon mode especially, which has been discussed in the neutron scattering experiments, is not a likely reason for this result, because the crossover between the ground state and a two-magnon binding state ($S^Z = 2$) must take place at the same or lower field than H_{c1}. This anomalous magnetization curve could be explained as a superposition of two magnetization curves for two different gap systems.

The observed critical phenomena are thought to be the crossover between the singlet ground state and the magnetic first excited state in each gap system with an independent gap energy. The gap energies between the singlet ground state and the triplet first excited state for both systems can be calculated to be $\Delta_I = g\mu_B H_{c1}/k_B = 33 \pm 1$ K and $\Delta_{II} = g\mu_B H_{c2}/k_B = 62 \pm 3$ K using a g value of 1.97 estimated from the X-band 9 GHz ESR measurements. The calculated lower energy gap Δ_I is in good agreement with the value determined from the inelastic neutron scattering experiments ($\Delta = 3.1$ meV = 36 K).

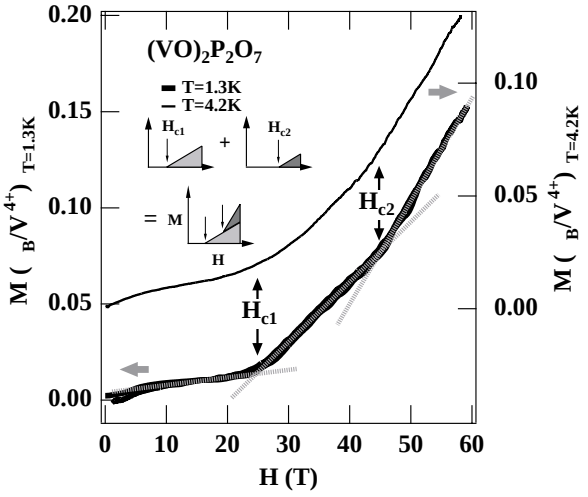

FIG. 2. The field dependence of the magnetization of $(VO)_2P_2O_7$. The slope of the magnetization curve clearly changes at $H = 25$ and 45 T as if two independent gap systems coexist in this compound, as schematically shown in the inset.

The higher gap Δ_{II} also coincides with that of the higher extra peak ($\Delta = 5.7$ meV $= 66$ K) in the inelastic neutron scattering spectra [4]. From these experimental results we propose the coexistence of the two gap systems with the different energy gaps in $(VO)_2P_2O_7$.

The slope of the magnetization curve in the intermediate field region ($H_{c1} < H < H_{c2}$) is about half of the slope in the higher field region ($H_{c2} < H$). This suggests that the volume fractions of each system are roughly equal under the condition that the dispersion relations of the magnetic excitations in each system are not significantly different. Now we can naturally attribute the two systems with the spin gaps to the chains A and B, because $(VO)_2P_2O_7$ consists of two kinds of alternating 1D Heisenberg $S = 1/2$ spin chains A and B which are equal in number and have similar magnetic-excitation dispersion relations observed in the neutron scattering experiments [4].

Coexistence of two different magnetic states in $(VO)_2P_2O_7$ has also been confirmed from ^{31}P NMR measurements. The field-swept NMR spectra of ^{31}P nuclei at various temperatures are shown in Fig. 3. The spectra have several lines which correspond to phosphorus atoms at crystallographically different sites. In the temperature region $30 \leq T \leq 100$ K, four lines $K_1 \sim K_4$ have been observed as shown in Fig. 3; nevertheless the eight P sites exist in the unit cell. At low temperatures ($T \leq 25$ K) the lines can be divided into two groups K_1, K_2 and K_3, K_4. Figure 4(a) shows the temperature dependence of the NMR shift in each resonance line obtained by deconvoluting the spectrum into four Gaussians. The shift of each group can be fitted to the conventional spin-gap formula $K_i - K_{\rm dia} = A_i \chi_{\rm spin}/g\mu_B\gamma_n\hbar \propto \exp(-\Delta/k_BT)/\sqrt{T}$ ($i = 1 \sim 4$) where A_i is a transferred hyperfine coupling constant for the peak K_i, which allows us to estimate the two gap energies $\Delta = 35 \pm 2$ K for K_1, K_2 and 52 ± 3 K for K_3, K_4, respectively. The results of the fitting are shown in Fig. 4(b). Note that the origin of the shift at the P sites is a transferred hyperfine field from the magnetic V^{4+} ions. Taking the superexchange interaction mediated by PO^4 tetrahedra as the transferred path, the eight different P sites can be naturally divided into the aforementioned two groups which are contained in chains A and B, respectively. The intensities of the NMR signals of each group are almost equal as seen in Fig. 3, which coincide with equal fraction of chains A and B in the structure. These NMR results support the double gap model in which chains A and B behave as the alternating spin chains with the independent gap energies.

The energy gaps estimated from three different experiments are summarized in Table I. They are in good agreement with each other except that the Δ_{II} in the NMR experiment is somewhat small compared to the other two. This discrepancy is probably due to a finite contribution to the shift at the P sites from the different kinds of chain [10]. The double gap behavior observed in $(VO)_2P_2O_7$

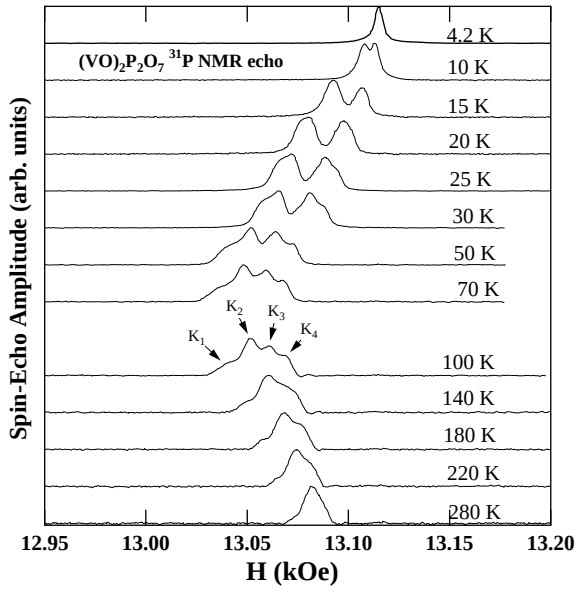

FIG. 3. The temperature variation of the field-swept ^{31}P NMR spectra taken at a fixed frequency of 22.6 MHz. The four lines $K_1 \sim K_4$ are clearly visible around 70 K.

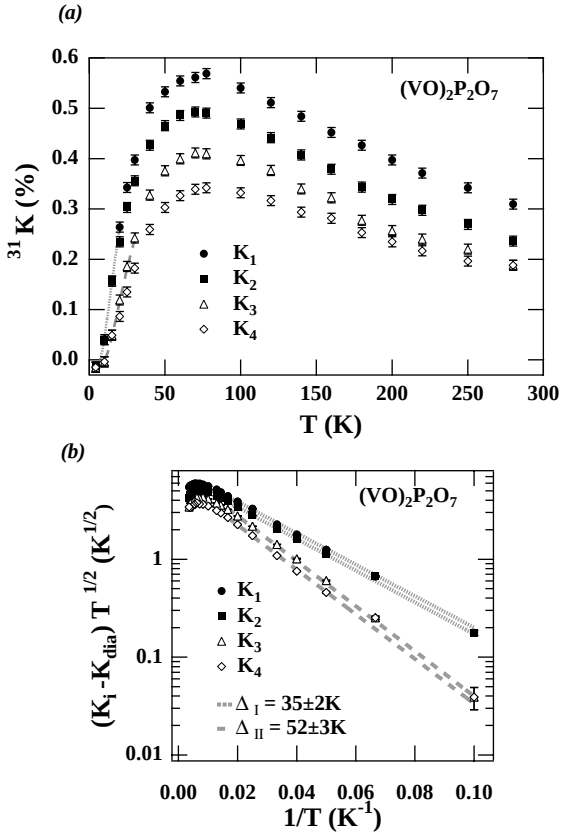

FIG. 4. (a) The temperature dependence of the NMR shifts of the four lines observed in ^{31}P NMR spin-echo spectra. (b) The gap behavior of the four lines. The four lines can be divided into two groups K_1, K_2 and K_3, K_4 from the temperature dependence of the shifts. Both groups show spin-gap behaviors with gap energies of 35 and 52 K, respectively.

TABLE I. Gap energies estimated from various experimental techiques. Values are given in degrees Kelvin.

	Neutron[a]	Magnetization	NMR
Δ_{I}	36	33 ± 1	35 ± 2
Δ_{II}	66	62 ± 3	52 ± 3

[a]Reference [4].

can be well explained by assuming that chains A and B behave as the alternating 1D Heisenberg $S = 1/2$ spin chains with the independent spin gaps. In previous studies chains A and B in $(VO)_2P_2O_7$ were considered to be the identical chains in magnetic properties.

We will show here that chains A and B cannot be regarded as identical and a difference of local crystal structure leads to a significant difference of the exchange interaction and therefore a significant difference of spin-gap behavior between the chains.

The exchange constants for chains A and B are represented by J_1^A, J_2^A, J_1^B, and J_2^B as shown in Fig. 1. We assume that chain A has the lower energy gap of 36 K and chain B has the higher energy gap of 64 K. The exchange constants for the chain with the gap energy of 36 K were previously calculated to be $J_1^A = 119$ K and $J_2^A = 101$ K from the neutron scattering experiments [4]. The neutron scattering experiments also show that the excitation energies of the two chains at the zone boundary are almost equal $(J_1^A + J_2^A)/2 \sim (J_1^B + J_2^A)/2 \sim 110$ K, and then we can calculate to be $J_1^B = 130$ K, $J_2^B = 90$ K for chain B with the higher energy gap [11]. Previously Millet *et al.* successfully estimated the exchange constants in vanadium compounds formed by edge/corner-shared VO_5 square pyramids, assuming that these depend only on the local geometry of the bonds; that is $J(d_{\mathrm{V\text{-}V}}) \propto (d_{\mathrm{V\text{-}V}})^{-10}$ for edge-shared VO_5 square pyramids where $J(d_{\mathrm{V\text{-}V}})$ is the exchange constant and $d_{\mathrm{V\text{-}V}}$ is the distance between V^{4+} ions [12]. By using their relation and the structural parameters, we can obtain the fact that the ratios of both the exchange constant and the bond distance between chains A and B are $J_1^B/J_1^A = 0.93$ (or $J_2^B/J_1^B = 0.87$) and $(d_{\mathrm{V\text{-}V}}^A/d_{\mathrm{V\text{-}V}}^B)^{-10} = 0.93$. A good agreement of the ratio between the exchange constant and bond distance shows that the difference of magnetic properties between chains A and B is significantly caused by the difference of the local crystal structure, although it cannot be specified which of J_1 and J_2 is the exchange constant between the edge-shared VO_5 pyramids. If each chain behaves as a non-interacting chain with independent gaps (the double gap model), the magnetic susceptibilities can be represented as the sum of the magnetic susceptibility of each chain. We tried to calculate magnetic susceptibility using the equation for the alternate chain [13] with the obtained parameters J_1^A, J_2^A, J_1^B, J_2^B, and g. The results are fitted to the observed magnetic susceptibility better in the double gap model than in the single gap model ($J_1^A = J_1^B$, $J_2^A = J_2^B$).

The spin gap system with an alternating one-dimensional Heisenberg $S = 1/2$ spin chain, $(VO)_2P_2O_7$, has been studied by the magnetization under high fields and ^{31}P NMR. Two critical phenomena at 25 ± 1 and 45 ± 1 T have been observed in the magnetization curve, which are considered to be the crossover between the ground state and the excited state in two kinds of gap system with the independent gap energies. ^{31}P NMR also revealed the coexistence of two magnetic systems with independent spin gaps. The results obtained from the present and previous studies are well explained by the model in which the two kinds of magnetic chains along the b axis behave as the alternating spin chains with the independent gap energies.

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