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LETTER TO THE EDITOR

NMR characterization of spin-$\frac{1}{2}$ alternating antiferromagnetic chains in the high-pressure phase of $(VO)_2P_2O_7$

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Abstract

Local-susceptibility measurements via the NMR shifts of ^{31}P and ^{51}V nuclei in the high-pressure phase of $(VO)_2P_2O_7$ confirmed the existence of a unique alternating antiferromagnetic chain with a zero-field spin gap of 34 K. The ^{31}P nuclear spin–lattice relaxation rate scales with the uniform spin susceptibility below about 15 K, which shows that the temperature dependences of both the static and dynamical spin susceptibilities become identical at temperatures not far below the spin-gap energy.

Magnetic excitations of a low-dimensional quantum antiferromagnet have been one of the current topics among condensed matter physicists. Vanadyl pyrophosphate $(VO)_2P_2O_7$ had long been believed to be a prototype of a spin-$\frac{1}{2}$ two-leg ladder which has a magnetic lattice intermediate between one and two spatial dimensions [1–5]. The ladder model, however, has been rejected by an observation of a dominant magnetic interaction perpendicular to the supposed ladder axis via the inelastic neutron scattering (INS) measurements [6]. A dimerized (alternating) chain model has now been becoming accepted as an alternative starting point, although a mechanism of the major exchange interaction between distant pairs of V^{4+} spins via PO_4 tetrahedra is still under study [7–9].

The INS experiments have also revealed the existence of a mode with a gap nearly twice the gap of the lowest excited triplet which cannot be explained by a simple alternating-chain model. This mode was first assigned as a bound state of two magnons possibly formed via interchain couplings [10], but it was difficult to account for the intensity, comparable to the fundamental mode. Recent NMR [11] and high-field magnetization [12] studies have suggested on this issue that the two structurally distinguishable chains of V atoms, which were

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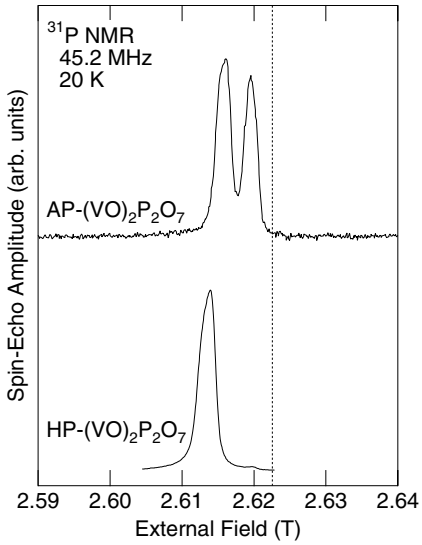

Figure 1. ^{31}P NMR spectrum in the ambient-pressure (upper panel) and the high-pressure (lower panel) phases of $(VO)_2P_2O_7$ at 20 K. The dotted line indicates the zero-shift position for ^{31}P.

thought to be magnetically identical, have different spin-gap energies. This gives a natural explanation for the existence of two distinct modes with almost equal spectral weight, and has been supported by the subsequent Raman-scattering experiments [13] and theoretical studies on relevant exchange interactions [7–9].

The above confusion concerning the modelling and interpretation of the experimental results of $(VO)_2P_2O_7$ comes not only from the unexpectedly strong V–V exchange via PO_4 tetrahedra, but also from the presence of structurally inequivalent V chains [14, 15]. More recently, Azuma *et al* [16] have found that $(VO)_2P_2O_7$ transforms into another phase with different symmetry under pressure. All the V atoms occupy a unique crystallographic site in the high-pressure (HP) phase, so that the magnetic chains made of V^{4+} spins are all equivalent. Therefore, HP-$(VO)_2P_2O_7$ will be a better example of the alternating antiferromagnetic chain with quantum spin $\frac{1}{2}$. In this letter, we report microscopic characterization of the magnetic chains in the HP phase of $(VO)_2P_2O_7$ via NMR. A single spin component characterized by a zero-field gap of 34 K was found, presenting support for the double-chain scenario for the ambient-pressure (AP) phase.

Single crystals of the HP phase of $(VO)_2P_2O_7$ were grown as described in [17]. Since the crystals were too small to observe an NMR signal, they were crushed into powders and the NMR measurements were made on these powders. Standard spin-echo pulse techniques were utilized for most of the experiments.

An example of the field-swept ^{31}P NMR spectrum in the HP phase of $(VO)_2P_2O_7$ is shown in figure 1. The spectrum in the AP phase [11] is also shown for comparison. The spectrum in the HP phase consists of a single line as expected from the unique crystallographic site of phosphorus in the unit cell. This is contrasted with the AP phase where the spectrum splits into two groups of lines owing to the presence of two kinds of V chain with different gap energies [11]. The line-shape analysis revealed that the symmetry of an NMR-shift tensor at the P site is almost uniaxial. Assuming the exact uniaxial symmetry, we determined the two independent principal values $K_\parallel$ and $K_\perp$ corresponding to the shift with the external field parallel and perpendicular to the local symmetry axis, respectively. The results are shown in

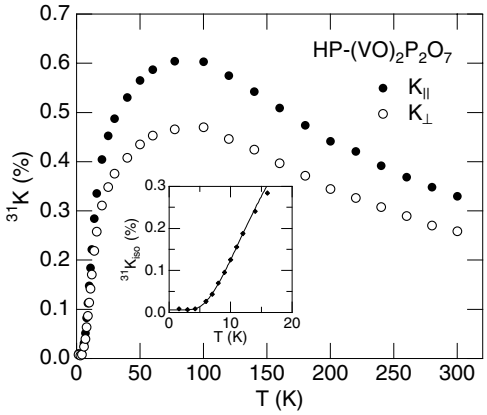

Figure 2. Temperature dependence of the principal values $K_{\parallel}$ and $K_{\perp}$ of the ^{31}P NMR-shift tensor in the high-pressure phase of $(VO)_2P_2O_7$. The inset shows the isotropic component of the NMR shift at low temperatures with the result of the fitting (solid curve).

figure 2 as a function of temperature. Both $K_{\parallel}$ and $K_{\perp}$ scale the bulk magnetic susceptibility χ which is corrected by subtracting the contribution of paramagnetic impurities. Following the standard K–χ analysis, the tensor components of the hyperfine coupling at the P site were determined as $A_{\parallel} = 2.19\ \mathrm{T}/\mu_{\mathrm{B}}$ and $A_{\perp} = 1.70\ \mathrm{T}/\mu_{\mathrm{B}}$. These values yield the isotropic and uniaxial components, $A_{\mathrm{iso}} = 1.92\ \mathrm{T}/\mu_{\mathrm{B}}$ and $A_{\mathrm{ax}} = 0.13\ \mathrm{T}/\mu_{\mathrm{B}}$, respectively. A_{ax} is larger than and different in sign from that due to the classical dipolar field of V^{4+} spins $A_{\mathrm{ax}}^{\mathrm{dip}} = -0.036\ \mathrm{T}/\mu_{\mathrm{B}}$, indicating that the V^{4+} spins are transferred not only to the P 3p orbitals but also to the P 3s orbital.

The susceptibility of a one-dimensional (1D) gapped spin system at temperatures well below the gap Δ is proportional to $T^{-1/2}\exp(-\Delta/T)$ [4]. In order to determine Δ, we fitted the T dependence of the isotropic component of the NMR shift $^{31}K_{\mathrm{iso}}$ below 10 K to the form $^{31}K_{\mathrm{iso}} = K_0 + \alpha T^{-1/2}\exp(-\Delta(H)/T)$, where the reduction of Δ by fields is explicitly written. The result is shown in the inset of figure 2. The obtained parameters are $K_0 = 0.006\%$, $\alpha = 0.081\ \mathrm{K}^{1/2}$, and $\Delta(2.62\ \mathrm{T}) = 31\ \mathrm{K}$ which gives $\Delta(0) = 34\ \mathrm{K}$ with the use of the measured g factor [17]. $\Delta(0)$ is in good agreement with that evaluated from the bulk χ but is larger than the values determined from the critical field of the magnetization process (∼23 K) [16] and the INS on polycrystals (∼25 K) [18] for unknown reasons.

A free-induction-decay (FID) signal of ^{51}V has also been observed below about 50 K. The spectrum was obtained by integrating the FID signal while sweeping the external field. The T dependence of the ^{51}V NMR shift ^{51}K determined from the peak position of the spectrum is shown in figure 3. Also shown in the inset is a plot of $^{31}K_{\mathrm{iso}}$ versus ^{51}K with T the implicit parameter. A linear relation found between $^{31}K_{\mathrm{iso}}$ and ^{51}K demonstrates that the T dependence of the local spin susceptibility is identical for both the sites. This is a clear sign of HP-$(VO)_2P_2O_7$ having only one independent spin component. The T dependence of ^{51}K was analysed in the same way as that of $^{31}K_{\mathrm{iso}}$ using Δ determined above. The T-independent orbital (van Vleck) shift was then obtained to be 0.182%. The hyperfine coupling constant at the V site determined from the slope of the ^{51}K–χ plot is $-14.8\ \mathrm{T}/\mu_{\mathrm{B}}$, which is in a reasonable range as a core-polarization field of a 3d transition-metal ion [19].

Figure 4 shows the T dependence of the ^{31}P nuclear spin–lattice relaxation rate $1/T_1$. T_1 above 8 K was determined as the time constant of the exponential recovery of ^{31}P magnetization $M(t)$. Below 8 K where non-exponential recovery appears, we analysed $M(t)$ by fitting to the

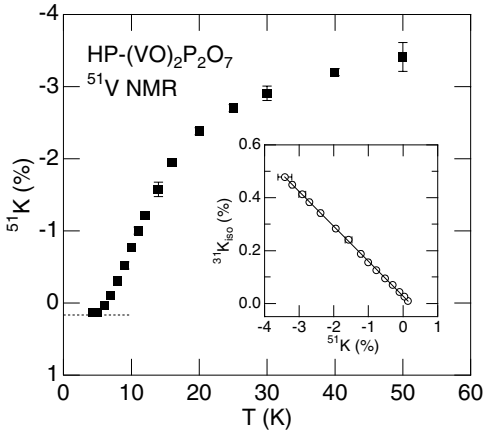

Figure 3. Temperature dependence of the ^{51}V NMR shift in the high-pressure phase of $(VO)_2P_2O_7$. The dotted line represents the orbital shift. The inset is a scaling of ^{51}K and $^{31}K_{\rm iso}$ plotted with temperature as the implicit parameter.

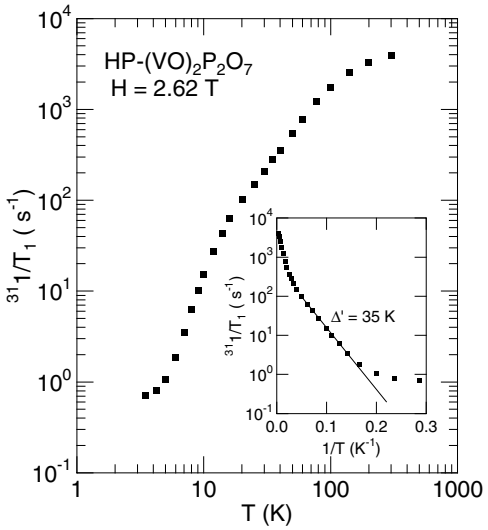

Figure 4. Temperature dependence of the ^{31}P nuclear spin–lattice relaxation rate $1/T_1$ in the high-pressure phase of $(VO)_2P_2O_7$. The inset is a semi-logarithmic plot of $1/T_1$ as a function of inverse temperature. The solid line in the inset shows the activation law $1/T_1 \propto \exp(-\Delta'/T)$ with $\Delta' = 35$ K.

form $1 - M(t)/M(\infty) \propto \exp(-t/T_1 - (t/\tau_1)^{1/2})$ which incorporates the relaxation rate $1/\tau_1$ due to paramagnetic impurities [20]. As shown in the inset of figure 4, $1/T_1$ exhibits activated behaviour below about 20 K. The exponential decrease of $1/T_1$ is, however, masked below $\sim$8 K synchronizing the appearance of non-exponential recovery. The asymptotic value of $1/T_1$ at low T is suppressed by applying fields as expected for the impurity-limited relaxation rate. $1/T_1$ depends on H at higher temperatures as well where the recovery is exponential, but the H dependence roughly follows the 1D diffusive form $1/T_1 \propto H^{-1/2}$ as observed in AP-$(VO)_2P_2O_7$ [21]. Details of the H dependence of $1/T_1$ will be presented in a separate paper. The activation energy was estimated as $\Delta' = 35$ K by fitting the data between 8 and

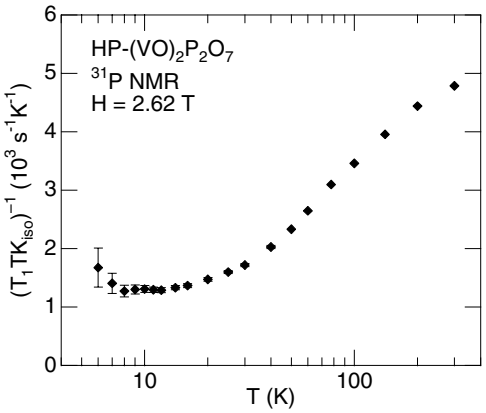

Figure 5. Temperature dependence of $(T_1TK_{\rm iso})^{-1}$ in the high-pressure phase of $(VO)_2P_2O_7$.

20 K to the form $1/T_1 \propto \exp(-\Delta'/T)$. As the interbranch ($\Delta S_z = \pm 1$) transitions within the lowest excited triplet [22] are expected to dominate the nuclear-spin relaxation due to the predominantly isotropic hyperfine fields, the obtained Δ' would give an estimate of the zero-field gap. Δ' indeed agrees well with $\Delta(0)$ evaluated from the NMR shift.

Figure 5 shows the T dependence of $1/T_1T$ divided by $K_{\rm iso}$. One of the remarkable features of the result is that the ratio $(T_1T)^{-1}/K_{\rm iso}$ becomes T independent below about 15 K. (An upturn below ~7 K is due to the impurity contribution to $1/T_1$ and is extrinsic.) It is well known that, while the NMR shift is proportional to the uniform static susceptibility $\chi'(0,0)$, $1/T_1$ samples the dissipative part of the dynamical susceptibility $\chi''(q,\omega)$ at the nuclear Larmor frequency $\omega_{\rm n}$ [23];

$$\frac{1}{T_1} = \frac{k_{\rm B}T}{2\mu_{\rm B}^2}\sum_q |A(q)|^2 \frac{\chi''(q,\omega_{\rm n})}{\omega_{\rm n}}.$$

Here $A(q)$ is the Fourier transform of the hyperfine coupling. Since $A(q)$ has a maximum at $q = 0$, $1/T_1$ at the P site is most sensitive to $\chi''(q \sim 0, \omega_{\rm n})$ which is dominant at low T in a gapped 1D spin system [4]. The T-independent behaviour of $(T_1T)^{-1}/K_{\rm iso}$ therefore indicates that the T dependences of $\chi''(q \sim 0, \omega_{\rm n})$ and $\chi'(0,0)$ at low T are identical and should be described by a common energy gap. Such a characteristic of the magnetic excitations in a gapped 1D spin system has been predicted theoretically based on a picture of free magnons [4], but has rarely been observed experimentally [24]. To our knowledge, this is the first experimental verification of $1/T_1T$ and K having identical T dependence at low T, not relying on any model-dependent form of these quantities. From the experimental viewpoint, it is worth noting that the scaling between $1/T_1T$ and K holds below $T \sim \Delta/2$. This suggests nearly free propagation of magnons being realized at temperatures not far below Δ. It is therefore practical to use experimental data in the region $T \leqslant \Delta/2$ for a reliable estimate of Δ, although the activated behaviour of physical quantities such as χ and $1/T_1$ is theoretically justified only for $T \ll \Delta$ [4].

Above about 20 K, the scaling breaks down and $(T_1TK_{\rm iso})^{-1}$ increases gradually with T. This means that $\chi''(q \sim 0, \omega_{\rm n})$ grows more rapidly than $\chi'(0,0)$. As the temperature is now comparable with or higher than Δ, interactions between magnons and/or the $q \neq 0$ component of spin fluctuations will become increasingly important and would enhance $\chi''(q,\omega)$ over $\chi'(0,0)$.

In conclusion, we have measured ^{31}P and ^{51}V NMR in the high-pressure phase of $(VO)_2P_2O_7$. It was found that the temperature dependence of the local static spin susceptibility

at the P site is identical with that at the V site. The dynamical spin susceptibility $\chi''(q, \omega)$ near $q = 0$ also scales with the static susceptibility at low temperatures below about one-half of the spin-gap energy which was estimated to be 34 K at zero field. All of these observations provide microscopic evidence for a unique kind of magnetic chain existing in the high-pressure phase of $(VO)_2P_2O_7$, as well as for coexistence of magnetically inequivalent chains in its ambient-pressure phase.

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