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# Observation of the Spin Gap in a $S = 1/2$ Alternating Chain Compound, High Pressure Phase of $(VO)_2P_2O_7$

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Inelastic neutron scattering data were collected on the high pressure phase of $(VO)_2P_2O_7$, a $S = 1/2$ Heisenberg antiferromagnetic alternating chain compound. The existence of a spin gap was confirmed, and the size was determined to be $\Delta$=2.15(6) meV (= 25.0(7) K). The theoretically predicted second gap ($\Delta$'=2$\Delta$) owing to a 2-magnon bound state was not observed. This is consistent with the high field magnetization measurement reported previously.

KEYWORDS: spin gap, alternating chain, $(VO)_2P_2O_7$, high pressure phase, neutron scattering

## §1. Introduction

Low dimensional magnets have been attracting much interest in recent years because of their exotic properties such as high-$T_c$ superconductivity in two dimensional (2D) $CuO_2$ planes and the presence of spin gaps in several one dimensional (1D) systems. 1D magnets are well studied theoretically.[1,2] Those with uniform antiferromagnetic (AF) interactions are known to have no energy gap in their magnetic excitation spectra, while those with alternating AF interactions have energy gaps called spin gaps between the singlet ground states and the lowest triplet excited states. Spin ladder systems with even legs also have spin gaps, and are expected to show high-$T_c$ superconductivity.[3–5]

Vanadium pyrophosphate $\alpha$-$(VO)_2P_2O_7$ (AP-VOPO) is a $S = 1/2$ Heisenberg AF alternating chain compound with $V^{4+}$ ($d^1$). It was first thought to be a typical realization of spin ladder system, but a neutron scattering study on single crystal samples revealed that the magnetic excitation is most dispersive in the direction perpendicular to the ladder direction.[6] The dominant AF interactions in this system are the one between a pair of $VO_5$ pyramids mediated by $PO_4$ tetrahedra (V-O-P-O-V; the strongest one, $J_1$) and one between a pair of edge-sharing $VO_5$ pyramids (V-O-V; the next strongest one, $J_2 < J_1$). The interaction along the ladder direction is very weak and may even be ferromagnetic.

Neutron scattering data also showed the existence of a second spin gap about twice as large as the first one, as predicted theoretically.[7] However, this compound comprises two slightly different chains,[8] making it difficult to determine whether these chains have single but different spin gaps, or have identical double gaps. $^{51}V$ and $^{31}P$ NMR and high field magnetization studies[9,10] showed that there are two different spin systems in AP-VOPO, each probably corresponding to the two crystallographically different spin chains. A recent numeric calculation study[11] on the magnetic susceptibility of a $S = 1/2$ Heisenberg AF alternating chain showed that the susceptibility data of AP-VOPO could be fitted well assuming the presence of two chains.[12] The estimated gap sizes, of 38.4 K (= 3.31 meV) and 67 K (= 5.8 meV), are in good agreement with the result of the neutron scattering study mentioned above.[6]

We found that AP-VOPO undergoes a morphological transformation into a high pressure phase (HP-VOPO) at 2 GPa and 700 °C.[13] HP-VOPO has an orthorhom-

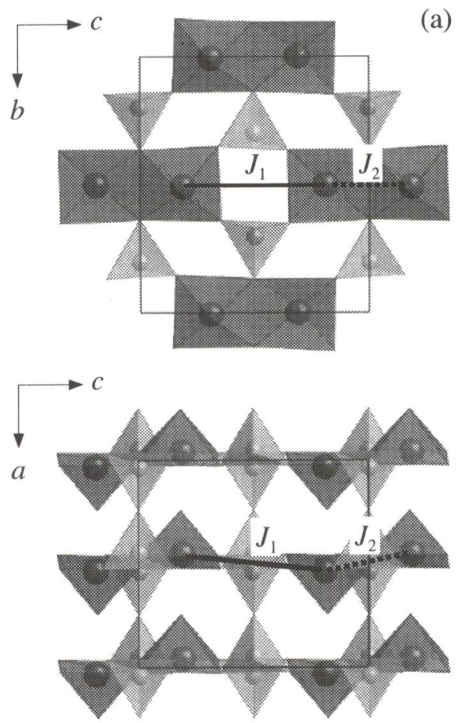


Fig. 1. Crystal structure of HP-VOPO viewed along the $a$-axis (a) and the $b$- axis (b). The big and small circles represent vanadium and phosphorous atoms, respectively. Oxygen atoms are located at the vertexes of the polyhedra. $J_1$ and $J_2$ ($J_1 > J_2 = \alpha J_1$) represent the superexchange interactions between $V^{4+}$ ions.

bic unit cell with lattice constants $a = 7.571$ Å, $b = 9.536$ Å and $c = 8.362$ Å.[14] The crystal structure of the HP phase, as illustrated in Fig.1, is similar to that of the AP phase, though the symmetry is higher in the former ($Pnab$) than in the latter ($Pca2_1$).[14] The HP phase consists of edge-sharing pairs of $VO_5$ pyramids and $PO_4$ tetrahedra, and both path ways for the two major AF interactions in the AP phase (V-O-P-O-V and V-O-V) are maintained in the HP phase. Because of these structural similarities, the AF interactions are likewise expected to be similar. In fact, magnetic susceptibility and magnetization data showed the existence of a spin gap.[13–15] The magnetic susceptibility data from a single crystal of HP-VOPO were fitted to the alternating chain model mentioned above.[11,12] $J_1$, $\alpha \equiv J_2/J_1$ and the spin gap size $\Delta$ were estimated to be 131.6 (1)K, 0.8709(5) and 33.4(2) K (= 2.87(2) meV), respectively. The size of the spin gap was also estimated from the magnetization curve of single crystals to be 22.9 K (= 1.973 meV), which is rather smaller than the result of the magnetic susceptibility study. In this paper, we report the results of an inelastic neutron scattering study on powder samples of HP-VOPO.

## §2. Experimental Details

AP-VOPO was prepared by the solid state reaction of $NH_4VO_3$ and $NH_4H_2PO_4$ . Stoichiometric amounts of these compounds were mixed, pressed into pellets and then heated at 550, 600, 700, and 750 °C successively for 12 hours each, and finally at 850 °C for 24 hours with intermediate grinding and pelletization. All these heat treatments were performed in flowing $CO_2$. Gold capsules ($\phi$ 10 mm × 17 mm) were filled with AP-VOPO powder, and then compressed in a conventional cubic anvil type apparatus to 3 GPa. It was then heated up to 800 °C at 140 °C/min, held at 800 °C for 30 minutes, and quenched to room temperature within a few seconds. The sintered sample thus obtained was ground into fine powder under an Ar atmosphere.

Inelastic neutron scattering experiments were carried out using the TOPAN triple-axis spectrometer installed in JRR-3 at the Japan Atomic Energy Research Institute. The HP-VOPO sample powder was sealed in 0.1 mm thick walled Al cylinders in a He filled glove bag. The weight of the samples were 8.6 g (sample I) and 23.0 g (sample II).

The horizontal collimator sequences were 80'-30'-30'-60' for sample I and 30'-30'-30'-30' for sample II with fixed neutron energy $E_i = 14.7$ meV.

## §3. Results

Since the sizes of the spin gaps obtained from the magnetic susceptibility and magnetization study were $\Delta_{chi} = 33.4(2)$ K (= 2.87(2) meV) and $\Delta_{MH} = 22.9$ K (= 1.973 meV), respectively, a constant-$Q$ scan of HP-VOPO powder was first performed, at energy transfer between these values, $dE = 2.5$ meV on sample I. The result is shown in Fig.2. A sharp peak can be seen at $Q = 0.75 \sim \pi/(c/2) \equiv Q_\pi$. This peak can be attributed to the excitation along the spin chain, because the average V-V distance along the chain is approximately $c/2$.

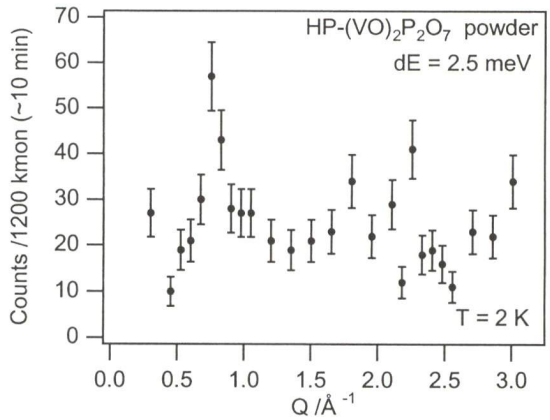


Fig.2. Constant energy scan of HP-VOPO powder sample at energy transfer $dE = 2.5$ meV. The measurements were done at 2 K with collimation 80'-30'-30'-60'

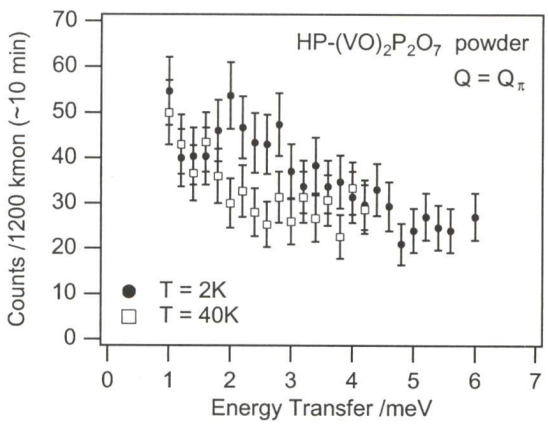


Fig.3. Inelastic scattering from HP-VOPO powder sample at temperatures of $T = 2$ K and 40 K. The measurements were done at $Q = 0.752$ Å$^{-1}$ with collimation 80'-30'-30'-60'.

In the elastic scattering measurement under 2 K, no change was found in the symmetry.

Therefore, a constant-Q scan was performed at $Q = 0.752$ Å$^{-1}$, corresponding to the AF zone center $Q = Q_\pi$. Figure 3 shows the data collected at $T = 2$ K and 40 K. A broad peak is clearly seen around 2 meV in the 2 K data. However, the peak has vanished in the 40 K data. This establishes that the peak is magnetic in origin, and corresponds to the singlet-triplet excitation over the spin gap. In contrast to the AP phase case, no extra peak was found at 2 K below 6 meV. This is consistent with the magnetization data which showed only one spin gap. In order to determine the size of the spin gap more accurately, additional constant-Q scans were performed on sample II at $T = 1.5$ K and 40 K between 0.6 and 4.0 meV. The result is shown in Fig.4 (a). The data collected at 40 K were subtracted from the 1.5 K data to make the peak clear. The subtracted differences could be well fitted to a Gaussian centered at 2.17(7) meV, which corresponds to 25.2(8) K, as shown in Fig. 3 (b).

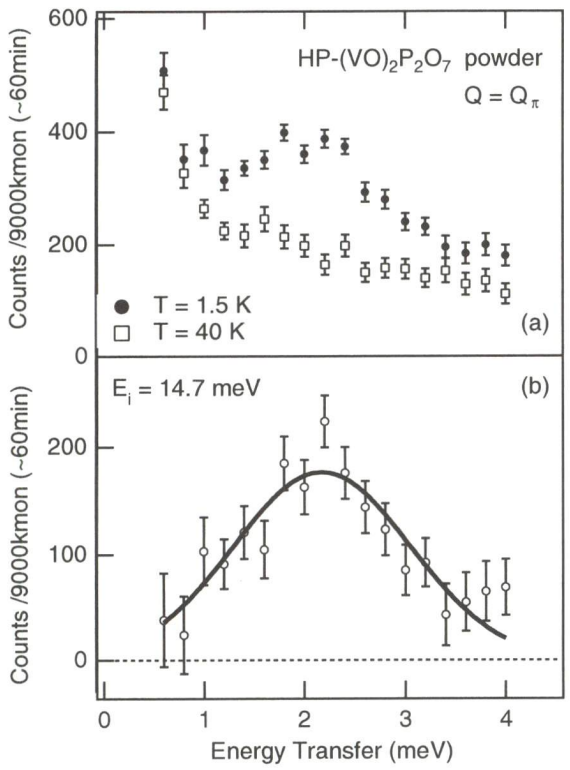


Fig. 4. Inelastic scattering from HP-VOPO powder sample at temperatures of $T = 1.5$ K and 40 K (a), and the subtracted difference (b). The solid line in (b) is a least-square fit of the difference to a Gaussian, with fitted center of 2.17(7) meV. The measurements were done at $Q = 0.755$ Å$^{-1}$ with collimation 30'-30'-30'-30'.

## §4. Discussions

Inelastic neutron scattering study on the HP-VOPO clearly showed the presence of only one spin gap, and the size of the gap was determined to be $\Delta_{INS} = 2.17(7)$ meV (= 25.2(8) K). This spin gap value is close to the one determined by the magnetization study ($\Delta_{MH} = 22.9$ K),[15] but is rather smaller than the one estimated by fitting the magnetic susceptibility ($\Delta_{chi} = 33.4$ K). The reason for this is not clear at this stage, but we propose two possibilities here. The spin gap size of an AF alternating chain is determined by the major AF interaction $J_1$ and the alternation $\alpha$. It is possible that these have a temperature dependence, as does the gap size. Since both inelastic neutron scattering and magnetization experiments were performed at a fixed temperature near 2 K, it is reasonable to expect that the sizes of the gaps obtained from these two experiments are quite similar. On the other hand, $\Delta_{chi}$ was estimated from the data collected over temperature range of $2 \sim 300$ °C.[12]

In the magnetic susceptibility, HP-VOPO has a 1D characteristic temperature dependence. However, there still is a possibility that the inter-chain spin interactions are not negligible, and that the size of the gap cannot be accurately estimated by fitting the magnetic susceptibility data. Neutron scattering studies on single crystals of HP-VOP we are preparing now will hopefully answer this question.

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