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Magnetism of a New Spin-1 Material $NaV(WO_4)_2$

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The magnetism of a new quantum-spin material $NaV(WO_4)_2$ is studied. The crystal structure shows a zig-zag $S = 1$ spin chain along the c axis. The magnetic susceptibility shows that the material has a spin gap. The exchange interaction and the energy gap are estimated to be $J = 180\,\mathrm{K}$ and $\Delta E = 26\,\mathrm{K}$, respectively. The possibility of a large next-nearest-neighbor interaction is discussed.

KEYWORDS: quantum spin systems, $S = 1$ zig-zag chain
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Quantum spin systems are among the most interesting physical models due to their simplicity. In some cases they can be solved numerically or even analytically and experimental results can reproduce theoretically predicted results. One of the most famous and successful examples is the Haldane gap[1] which is observed in a one-dimensional $S = 1$ spin model. The Haldane conjecture, which predicted the existence of a spin gap and the exponential decay of the spin correlation function, was justified by numerical calculation[2] and explained analytically by the use of an approximate model, the valence bond solid model.[3] Many experimental results also justified the conjecture.[4,5]

Recently, $S = 1$ spin chain with the next-nearest-neighbor interaction was studied theoretically.[6–9] The rich phase diagram of the ground state in the $S = 1$ chain with a single-ion anisotropy was obtained theoretically,[9] but to date only a few materials has been reported experimentally.[10] Candidate model compounds may be found among zig-zag chains. $NaR^{3+}(WO_4)_2$ (R = In, Sc[11] $S = 0$, Cr[12] $S = 1/2$ or $3/2$, and V[13] $S = 0$ or 1) are isostructural with each other. The crystal structure is monoclinic and the space group is $P2/c$. Figure 1 shows the crystal structure of $NaIn(WO_4)_2$,[11] which had been studied in the most detail among the materials in $NaR^{3+}(WO_4)_2$ family. The zig-zag chains of the edge-shared InO_6 octahedra are extended along the c axis and are separated by the zig-zag chains of NaO_6 octahedra and large W^{6+} ions. The zig-zag angle ∠ In–In–In is 98.7°.

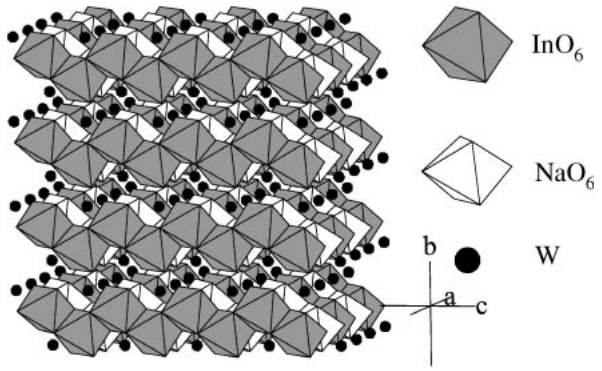

Fig. 1. Crystal structure of $NaIn(WO_4)_2$ which is isostructural with $NaV(WO_4)_2$. Zig-zag chains of InO_6 and NaO_6 octahedra are along the c axis. This figure is drawn according to the crystal data in ref. 11.

The lattice constants and the angle β are $a = 10.08\,\text{Å}$, $b = 5.81\,\text{Å}$, $c = 5.03\,\text{Å}$, and $\beta = 90 \pm 0.5°$. The magnetic susceptibility in $NaCr(WO_4)_2$ was reported[12] and the qualitative behavior showed that the model Hamiltonian in this material can be described by a low-dimensional spin model. The spin state V^{3+} ($3d^2$) is $S = 1$ in the case of a high-spin state and $S = 0$ in the case of a low-spin state. Therefore, the $S = 1$ low-dimensional spin model is expected for $NaV(WO_4)_2$ if the spin state of V^{3+} is the high-spin state. In this material, the lattice constants and the angle β are $a = 9.880\,\text{Å}$, $b = 5.698\,\text{Å}$, $c = 4.987\,\text{Å}$, and $\beta = 90.25°$.[13] A strong next-nearest-neighbor interaction is expected based on the crystal structure. In this paper, we report the magnetic susceptibility measurement in $NaV(WO_4)_2$.

A polycrystalline $NaV(WO_4)_2$ sample was prepared in two steps. The first step was the solid-state reaction method. The starting materials used were $NaCO_3$, V_2O_3, and WO_3. A mixture of them placed in an evacuated quartz tube was heated in a furnace up to 800°C for 200 h. Intermediate regrinding was required. The second step was the flux method. An appropriate mixture of $NaV(WO_4)_2$, which was obtained in the first step, and $Na_2W_2O_7$ was heated to 1000°C. The mixture was kept at this temperature for 24 h, cooled at the rate of 2°C/h to 650°C, and at 5°C/h to room temperature. The solvent $Na_2V_2O_7$ was removed in boiling water. A dark brown needle-shaped single crystal was obtained. The single crystals were too small for the measurement of the magnetic susceptibility. We then ground them and obtained a high-quality polycrystalline sample.

The magnetic susceptibility measurement was performed using a commercial SQUID magneto-meter (MPMS, Quantum Design Co., Ltd.).

Figure 2(a) shows the magnetic susceptibility of $NaV(WO_4)_2$. The magnetic susceptibility has a strong temperature dependence, which means that the spin state of V^{3+} ions is magnetic, i.e., a high-spin state, and $S = 1$ spins are localized at the ions. A broad maximum, which is due to antiferromagnetic fluctuation, is observed at $T \sim 200\,\mathrm{K}$ and this means that the model Hamiltonian can be described by a low-dimensional quantum spin model. A decrease in the susceptibility at lower temperature is observed, though the Curie-like behavior is observed at a very low temperature. The minimum value of the susceptibility ($T \sim 10\,\mathrm{K}$) is about half the maximum value ($T \sim 200\,\mathrm{K}$) in this material. The decrease of the suscept-

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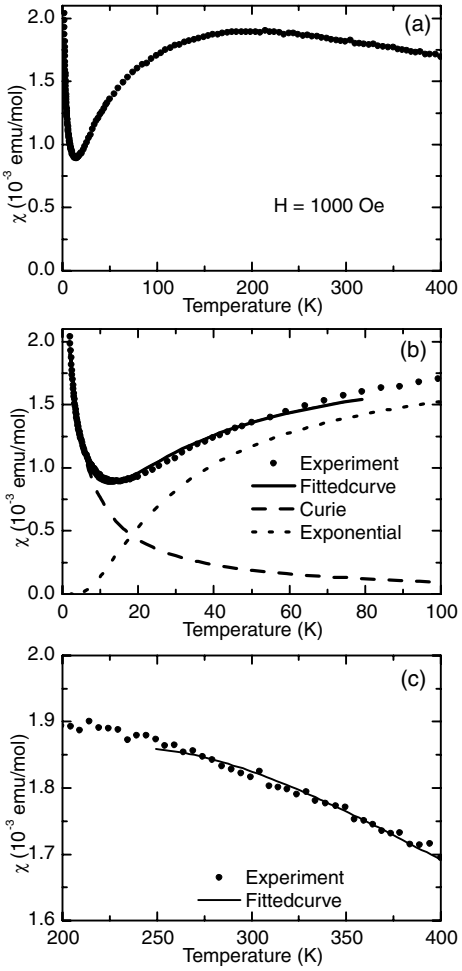

Fig. 2. (a) The magnetic susceptibility in $NaV(WO_4)_2$. (b) The fit to the data below 75 K by Curie and exponential decay curves. (c) The fit to the data at 250 K $\lesssim T$ by high-temperature expansion.

ibility is more significant than that in a gapless one-dimensional quantum spin model. In the case of the $S = 1/2$ spin system, for example, the ratio of the minimum to the maximum value of the susceptibility is about 0.7.[14] No anomaly due to a phase transition is observed down to 2 K. Therefore, we concluded that this material has a spin gap.

In Fig. 2(b), we fit the data to,

$$\chi = \frac{C}{T-\theta} + A\exp\left(-\frac{\Delta E}{k_B T}\right). \quad (1)$$

The obtained energy gap and Curie constant are $\Delta E = 26.4\,\mathrm{K}$ and $C = 10.0 \times 10^{-3}$ emu K/mol, respectively. The effective number of impurity spins, x, was estimated from the Curie constant and $x = 1.0\%$ under the assumption that $S = 1$ and $g = 2$. The V^{3+} ion is easily oxidized and the valence number easily changes, which may be the reason for the spin impurity. The V^{4+} ion, for example, would induce a free $S = 1/2$ spin.

The spin interaction, assuming the Heisenberg model, is estimated by high-temperature expansion.[15] The fitting equation is

$$\chi = \frac{\mu_B^2 g^2 N}{k_B T} \frac{2 + 0.0194\left(\frac{J}{T}\right) + 0.777\left(\frac{J}{T}\right)^2}{3 + 4.346\left(\frac{J}{T}\right) + 3.232\left(\frac{J}{T}\right)^2 + 5.834\left(\frac{J}{T}\right)^3}. \quad (2)$$

The fit to the experimental data is shown in Fig. 2(c). $g = 2.3$ and $J = 180\,\mathrm{K}$ are obtained. To estimate the exact value of J, we should consider anisotropy, interchain interaction, and next-nearest-neighbor interaction. However, fitting equation which includes all of them has not been reported and we adopted the fitting equation based on the simplest Heisenberg Hamiltonian here.

In the 1D $S = 1$ Heisenberg model, the relation between the energy gap and the exchange interaction is $\Delta E \cong 0.41J$.[16,17] Generally the Haldane gap is defined as the gap at the antiferromagnetic zone center, but in the following discussion, we define ΔE as the spin gap in the global reciprocal lattice. The reason is that we estimated ΔE from the magnetic susceptibility measurement. In $NaV(WO_4)_2$, the relation is $\Delta E = 0.15J$ and the energy gap is significantly suppressed. There are three possible causes for the suppression of the energy gap, i.e., the single-ion anisotropy D, the interchain interaction J_{inter}, and the next-nearest-neighbor interaction J_{NNN}. In the quasi-1D antiferromagnets reported so far, the next-nearest-neighbor interaction was neglected because the spin chain is almost linear. The relation between the energy gap and the single-ion anisotropy was reported in refs. 16 and 17, and the J_{inter}–D phase diagram and experimental results are summarized in Fig. 1 in ref. 18. NENP has a relatively large D in the $S = 1$ quasi-1D antiferromagnet; it has the largest D in Fig. 1 in ref. 18. Even in NENP, the relation between ΔE and J is $\Delta E = 0.22J$.[4] Here ΔE is the minimum energy gap between singlet ground state and the lowest excited state in the global reciprocal lattice. The discrepancy in the relation is larger for $NaV(WO_4)_2$.

In $NaV(WO_4)_2$, the spins form a zig-zag chain and a strong next-nearest-neighbor interaction is expected. If the next-nearest-neighbor interaction is antiferromagnetic, $NaV(WO_4)_2$ would be a model for a frustrated $S = 1$ chain. In this case the relation, $\Delta E = 0.15J$, does not have qualitative meaning because we adopted the fitting equation based on the simplest Heisenberg model. The antiferromagnetic NNN interaction suppresses the antiferromagnetic short-range order and broad maximum in the magnetic susceptibility shifts to a low temperature with the increase of J_{NNN}. In $CuGeO_3$, for example, $J = 88\,\mathrm{K}$ based on the simple Heisenberg model[19] and $J = 150\,\mathrm{K}$ based on the NNN interaction model.[20] We can say that $J = 180\,\mathrm{K}$ is underestimated by use of eq. (2) and the coefficient 0.15 in the relation between J and ΔE is smaller if we consider the NNN interaction.

The ground state of the $S = 1$ spin chain with NNN interaction has been studied theoretically.[6–9,21] If the exchange interaction is isotropic and the single ion anisotropy is absent the energy gap increases first, and then, decrease with increasing next-nearest-neighbor interaction strength.[21] At $\alpha \equiv J_{\mathrm{NNN}}/J \cong 0.74$ the ground state changes to "double Haldane phase." If the exchange interaction is *XXZ* model-like[7,8] or the exchange interaction is an isotropic Heisenberg model and a single-ion anisotropy is present,[9] the existence of "gapped and gapless chiral phases" is proposed. The phase is novel in that the order parameter is a chirality, $\kappa_l = S_l^x S_{l+1}^y - S_l^y S_{l+1}^x$. Because of the existence of the novel phase, the spin gap in the quasi-1D antiferromagnet with the next-nearest-neighbor interaction and with the single-ion anisotropy will be suppressed.

The relation between ΔE and J in $NaV(WO_4)_2$ indicates the suppression of the Haldane gap. The suppression of the spin gap might be explained only by the interchain interaction or the single-ion anisotropy, but the crystal structure indicates the existence of the next-nearest-neighbor interaction. Therefore, another possible explanation for the suppression of the Haldane gap in $NaV(WO_4)_2$ is that the theoretically predicted gapped and gapless chiral phases or double Haldane phase exist and the ground state of this material is close to these phases.

We found a new spin-gap material, $NaV(WO_4)_2$. The spin chain is zig-zag and the possibility of a frustrated $S = 1$ chain in this material is discussed. The estimation of D by magnetization measurement will be necessary in the future. The experiments on materials of the $NaV(WO_4)_2$ family may lead to the discovery of gapped and gapless chiral phases or double Haldane phase.

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