Spin-Singlet State in Sb$_2$VO$_5$

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Abstract. We have measured the high-field magnetization of a quasi-one dimensional $S=1/2$ chain compound Sb$_2$VO$_5$, which was proposed as a new candidate of the inorganic spin-Peierls (SP) system. The magnetization measured at 4.2 K exhibits a clear inflection at around 23 T, indicating obviously the excitation from a spin singlet ground state to a triplet state. Absence of anomalies in specific heat and X-ray diffraction points to no SP transition, and the analysis of the susceptibility suggests that this compound is an alternating spin chain system.

1. Introduction
The spin-Peierls (SP) transition is one of interesting topics in the one-dimensional (1D) antiferromagnetic Heisenberg spin system. Since CuGeO$_3$ is an only established inorganic compound which shows SP transition[1], new candidate materials have been searched so far. Pashchenko and his collaborators proposed that Sb$_2$VO$_5$ is a new SP compound with $T_{SP}=13$ K based on magnetic susceptibility $\chi$ and ESR measurements[2]. The crystal structure of Sb$_2$VO$_5$ (stibivanite) is monoclinic with space group $C2/c$ at room temperature. V$^{4+}$O$_4$ pyramids link to neighboring pyramids with sharing two edges of both sides, so that they construct a quasi-1D uniform chain along $c$ axis[3, 4]. At high temperatures, $\chi$ of Sb$_2$VO$_5$ takes a broad maximum at around 160 K and its temperature dependence above 60 K is well described by the $S=1/2$ 1D antiferromagnetic Heisenberg model with exchange interaction $J/k_B \approx 250$ K. With decreasing temperature $\chi$ shows a sudden drop at about 40 K, which was believed to be a sign of pseudogap formation. From the temperature dependence of $d\chi/dT$ and divergent increase of linewidth of the ESR spectrum, the SP transition temperature was determined to be $T_{SP}=13$ K[2].

However, the nonmagnetic ground state still remains to be confirmed because impurity contribution masks the low-temperature $\chi$ and ESR spectrum. Any undoubted evidence of the transition such as a cusp of $\chi$, new Bragg peaks or new phonon modes has not been observed either[2]. To reveal the ground state of Sb$_2$VO$_5$, we have measured high-field magnetization together with susceptibility, specific heat and low-temperature X-ray diffraction (XRD).

2. Experiments
Polycrystalline samples used for measurements were prepared by solid state synthesis from powders of Sb$_2$O$_3$, V$_2$O$_3$ and V$_2$O$_5$. These starting materials were ground in an agate mortar,

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pressed into 6 mm diameter pellets and then sealed in evacuated silica tubes. Heat treatment was performed at 550°C for 2 days with intermediate regrinds. The obtained samples were found to be in a single phase by powder XRD measurements. The temperature dependence of χ of the obtained samples measured with a Quantum Design MPMS reproduces well literature data[2]. The high-field magnetization measurement was performed at 4.2 K up to 55 T with a pulse magnet equipped at ISSP, University of Tokyo. The specific heat was measured in the temperature range from 0.5 to 50 K with a Quantum Design PPMS in zero magnetic field. The low temperature XRD pattern was obtained with Cu-Kα radiation (Mac Science M18XHF22).

3. Results and Discussion

![Figure 1](image_url)

**Figure 1.** The magnetization of Sb$_2$VO$_5$ at 4.2 K. Thin and thick lines represent the raw and impurity-corrected data, respectively. The dashed lines mean the extrapolation below and above $H_c$.

The result of the magnetization measurement at 4.2 K is shown in figure 1. The magnetization increases convexly at low fields and turns to increase rapidly above 20 T. The convex part at low fields is attributed to magnetic impurity, and then should be subtracted. We fit the magnetization below 15 T with a function $M(H) = f_{\text{imp}}N_A\mu_BSB_S(g\mu_BSH/k_BT) + aH$, where $f_{\text{imp}}$, $N_A$, $g$, $\mu_B$, $B_S$, and $a$ are the fraction of impurity moments, Avogadro’s number, $g$-value, Bohr magneton, the Brillouin function and the coefficient of the field-linear term, respectively. For the fitting, we assumed $g=2$ and $S=1/2$. The obtained magnetization is well fitted with the above function. The estimated fraction of impurity $f_{\text{imp}}=7.8 \times 10^{-3}$ is very small and is the same order of that estimated in the reference[2]. In the figure we plot the corrected magnetization. Above the inflection around 20 T, the magnetization increases linearly, and reaches 5% of the full moment for $S=1/2$ spin (1$\mu_B$) at 55 T. Extrapolating the magnetization below and above the inflection, $H_c$ is estimated to be 23 T at 4.2 K. This behavior corresponds to excitation from a nonmagnetic state to a paramagnetic one, namely a gapped spin-singlet ground state of Sb$_2$VO$_5$.

Although the spin-singlet ground state is no doubt, the magnetization of Sb$_2$VO$_5$ is qualitatively different from those observed for conventional SP compounds at low temperatures. In CuGeO$_3$ and organic SP compounds, the magnetization shows a stepwise jump at $H_c$ well below $T = T_{SP}[5, 6]$. On the other hand, the magnetization in our system shows smooth increase at $H_c$. This behavior is commonly observed in interacting dimer systems with a finite spin gap, such as TlCuCl$_3$ and KCuCl$_3[7]$. 
Field induced phases of SP compounds and interacting dimer systems are qualitatively different from each other. In the case of CuGeO$_3$, an antiferromagnetic soliton lattice with structural modulation is induced due to the strong spin-phonon coupling[8, 9]. On the other hand, in the interacting dimer system, an antiferromagnetically ordered phase with transverse components is observed, which is recently called as the magnon Bose-Einstein condensation state[10]. $H_c$ does not correspond to the spin gap energy in the former case, whereas they agree in the latter. When we apply the BEC picture, the value of $H_c$ corresponds to that of spin gap energy with the relation $\Delta(0) = g\mu_B H_c(0)$ at $T=0$ K because the energy of one of excited triplet states decreases as $-g\mu_B H$ with increasing field and crosses that of the singlet state at $H_c$. Using $H_c=23$ T at 4.2 K, we estimate the spin gap energy of this system as $\Delta/k_B = 31$ K.

In figure 2, we show the temperature dependence of specific heat divided by temperature $C/T$ up to 50 K. There are no apparent anomalies around $T=13$ K at which the SP transition is suggested to occur. No other anomalies were observed up to $T=50$ K either. We performed conventional XRD analyses below and above the suggested $T_{SP}$ (at 7 K and RT). At 7 K, we have observed no extra peaks within the experimental accuracy.

Taking the CuGeO$_3$ case into consideration, in which the structural transition was not noticed in the first report[1] due to its so slight structural modulation, it may not be unreasonable that extra Bragg peaks have not been observed by the conventional XRD. On the other hand, if the system actually underwent the SP transition, the absence of anomalies in the specific heat is rather unexpected.

From these experimental results, we conclude as follows: 1) the magnetic ground state is spin singlet, 2) there is no phase transition either at 13 K or up to 50 K. The latter conclusion does not necessarily contradict with the previously reported data, where no apparent phase transition has been detected[2]. $T_{SP}$ determined from the peak of $d\chi/dT$ may be an experimental artifact. If that is the case, how could Sb$_2$VO$_5$ be in the spin singlet state? Judging from the behavior of the magnetization, the SP scenario is unsuitable for Sb$_2$VO$_5$. As another possibility, we apply the $S=1/2$ 1D alternation chain model[11], because the whole temperature dependence of $\chi$ can well be fitted with the following function as shown in figure 3; $\chi(T) = \chi_{alt}(\alpha, T) + C/(T - \theta) + \chi_0$, where

$\alpha = 0.92$, $C = 0.0035$, $\theta = -0.79$ K, $\chi_0 = 0.175 \times 10^{-3}$ emu/mol

$J/k_B = 232$ K

$C/k_B = 0.0035$, $\theta = -0.79$ K

$\chi_0 = 0.175 \times 10^{-3}$ emu/mol
where $\chi_{\text{alt}}$ is the susceptibility with the $S=1/2$ alternating chain model, $\alpha = J_2/J_1$ is the alternation parameter ($\alpha=0$ corresponds to the isolated dimer case and $\alpha=1$ uniform chains. In the case of $0 \leq \alpha < 1$, the ground state is a gapped spin singlet.). $J_1$ and $J_2$ are stronger and weaker interaction constants, $C$ and $\theta$ are Curie and Weiss constants of impurity, and $\chi_0$ is a temperature independent term. Although the reported crystal structure consists of uniform chains, the structural modulation would be small if any because the obtained alternation parameter $\alpha=0.92$ is close to 1. In the present stage, the origin of the spin singlet formation in Sb$_2$VO$_5$ is still remains to be elucidated. The further study is needed.

4. Conclusion
We have measured high-field magnetization, specific heat and low temperature XRD of a quasi-1D compound Sb$_2$VO$_5$. The existence of spin gap was confirmed by the high-field magnetization measurement. Specific heat and XRD measurements show no sign of the SP transition suggested in the previous paper at 13 K. The susceptibility can well be reproduced by the $S=1/2$ alternating spin chain model.

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