Magnetic properties of $S=1/2$ $J_1$-$J_2$ one-dimensional magnets, VO(XO$_4$)(2,2’-bpy) (X=S, Mo; bpy = bipyridine)

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Abstract. Magnetic susceptibility, high field magnetization and specific heat of $S=1/2$ $J_1$-$J_2$ spin chain compounds VO(XO$_4$)(2,2’-bpy) (X=S, Mo; bpy = bipyridine) are measured. VO(SO$_4$)(2,2’-bpy) is found to be a one-dimensional Heisenberg antiferromagnet with $J_1/k_B=6.5$ K and $J_2=0$. A ratio $j=J_2/J_1$ of VO(MO$_4$)(2,2’-bpy) is estimated to be about 0.2 with $J_1/k_B=51$ K. Spin gap is not observed in both the compounds, which is consistent with the theoretical prediction.

1. Introduction

One dimensional Heisenberg antiferromagnets (1D HAF) with the nearest $J_1$ and the second-nearest $J_2$ interactions ($J_1$-$J_2$ model or zigzag chain model) are the simplest frustrated magnets. Because several interesting magnetic phases[1], including the nematic spin phase[2], are predicted to be realized in the $J_1$-$J_2$ model with $S=1/2$, several experimental and theoretical works on $J_1$-$J_2$ model have been conducted. Given the fact that the quantum phase transitions are mainly determined by the relative ratio of $J_1$ of $J_2$, actual model compounds with different parameters are required to perform experimental studies on the ground state phase diagram.

The V$^{4+}$ ions ($S=1/2$) in VO(XO$_4$)(2,2’-bpy) (X=S, Mo; bpy = bipyridine) [3] form double chain such that these compounds can be regarded as new materials for the $J_1$-$J_2$ model (Fig. 1). The exchange interactions between the V$^{4+}$ ions in each compound are assumed to be mediated through the XO$_4$ ionic group. We have already reported the measurement results of magnetic susceptibility and high field magnetization of up to 35 T of VO(MO$_4$)(2,2’-bpy) [4]. However it was not possible to accurately determine the values of exchange coupling, because of the masking by magnetic impurities and very large saturation magnetic field.

In the present study, we report the results of magnetic susceptibility, high field magnetization up to about 60 T and specific heat of VO(XO$_4$)(2,2’-bpy). In addition, we discuss the determination of the exchange coupling constants of these compounds.
2. Experiments
Powder samples of VO(XO$_4$)(2,2'-bpy) were synthesized by hydrothermal method, according to the procedure reported in Ref. 3. The quality of the specimen was investigated by powder X-ray diffraction. All the measurements were performed using the prepared powder samples. Magnetic susceptibility was measured using a SQUID (superconducting quantum interference device) magnetometer (MPMS, Quantum Design) in the temperature range of 2 - 300 K. High-field magnetizations of up to 60 T were measured using a pulsed high magnet at the Institute for Solid State Physics. Specific heat measurements were performed using a Quantum Design PPMS by the relaxation method under an applied field of up to 7 T.

3. Results and Discussion
The following sections present the measurement results of VO(SO$_4$)(2,2'-bpy) and VO(MoO$_4$)(2,2'-bpy), and the corresponding discussion and analysis.
3.1. VO(SO$_4$)$_2$(2,2'-bpy)

Figure 2 shows the temperature dependence of the magnetic susceptibility of VO(SO$_4$)$_2$(2,2'-bpy) measured at 100 Oe. The inset indicates the temperature dependence of the reciprocal susceptibility. A fit of a high temperature region of $\chi(T)$ to the Curie-Weiss law yields an antiferromagnetic Weiss temperature of $\Theta = -30$ K. A broad peak observed at 4.1 K confirms the one-dimensional nature of this compound. Magnetic susceptibility of the $S = 1/2$ $J_1$-$J_2$ model was calculated using the density-matrix renormalization-group method [5]. Best-fit results of the calculation to the experimental data are obtained for $J_1/k_B=6.5$ K and $j$ ($=J_2/J_1$) = 0, as indicated by a solid line in Fig. 2. Furthermore, the Lande’s $g$ value is estimated to be 1.85,
Figure 5. The temperature dependence of the magnetic susceptibility of VO(MoO$_4$)(2-2’-bpy). Theoretical calculation for $J_1/k_B = 51$ K and different values of $j = 0-0.3$ are plotted.

Figure 6. High field magnetization of VO(MoO$_4$)(2-2’-bpy) measured at 1.3 K up to 60 T. The solid line is the calculated magnetization with $J_1/k_B = 51$K and $j = 0.2$.

Figure 7. The temperature dependence of the specific heat of VO(MoO$_4$)(2-2’-bpy).

which is consistent with the reported values 1.925-1.976 as determined by the ESR experiment [6]. Given the ratio parameter $j = 0$, VO (SO$_4$)(2,2’-bpy) is described as a simple HAF rather than the $J_1$-$J_2$ model material. Figure 3 shows the high field magnetization curve measured at 1.3 K. The magnetization curve exhibits a down-convex form, which is commonly observed in the magnetization of 1D HAF. The field derivative of the magnetization $dM/dH$ has a peak at around 9 T, which is the saturation magnetic field. The theoretical curve at $T=0$ calculated for 1D HAF without $J_2$ [7] agrees well with the experimental data as shown in Fig. 3. Figure 4 shows the temperature dependence of specific heat measured at different fields up to 7 T. The lattice contribution is not subtracted because an isostructural compound without magnetic ions is not known. A broad peak is observed in the specific heat measured in zero field at around
3.5 K, which corresponds to the temperature at which $\chi(T)$ is the maximum. Inset shows the magnetic field dependence of the peak temperature of specific heat. Upon increasing the applied field, the peak temperature monotonically decreases.

3.2. VO(MoO$_4$)(2,2'-bpy)

Figure 5 shows the temperature dependence of $\chi(T)$ of VO(MoO$_4$)(2,2'-bpy). A broad maximum is observed at around 40 K, which is higher than that observed for VO(MoO$_4$)(2,2'-bpy). Low temperature upturn is because of a small amount of magnetic impurities. Given the fact that the simple 1D HAF model is insufficient to fit the experimental data, finite $J_2$ is suggested to be present in this compound. We thus made an attempt to obtain the best-fit for the experimental data. Although quantitative fitting is not obtained, the experimental data qualitatively agree to the theoretical curve for $J_1/k_B = 51$ K and $j = 0.2$, as plotted in Fig. 5. Figure 6 shows the high field magnetization curve measured at 1.3 K. As expected from large exchange constant $J_1$, magnetization does not attain its saturation value of 1 $\mu_B$ even at the highest field of 60 T. Using the parameters determined from $\chi(T)$ $J_1/k_B = 51$ K and $j = 0.2$, we calculated the theoretical magnetization curve, as shown in Fig. 6, which agrees to the experimental data. Figure 7 shows the temperature dependence of specific heat at zero field. Here, the lattice contribution is not subtracted.

No anomaly associated with the magnetic phase transition was observed despite the large values of the exchange constant. This implies that VO(MoO$_4$)(2,2'-bpy) has good one-dimensionality. Spin gap is not observed both in the magnetization and the specific heat data. The gapless behavior for the $J_1$-$J_2$ spin chain with $j = 0.2$ is consistent with the theoretical expectation that the quantum phase transition occurs at $j_c = 0.2441$ from gapless spin fluid to the gapped dimer phase with an increase in $j$ from 0 [8]. It is found that the ground state of VO(MoO$_4$)(2,2'-bpy) belongs to the gapless spin fluid phase.

4. Conclusion

In summary, we have determined the magnetic susceptibility, high-field magnetization and specific heat of $S = 1/2$ $J_1$-$J_2$ spin chain compounds VO(XO$_4$)(2,2'-bpy) (X = S, Mo; bpy = bipyridine). VO(SO$_4$)(2,2'-bpy) is found to be a one-dimensional Heisenberg antiferromagnet with $J_1/k_B = 6.5$ K and $J_2 = 0$. The ratio $j = J_2/J_1$ of VO(MoO$_4$)(2,2'-bpy) is estimated to be about 0.2 with $J_1/k_B = 51$ K. Spin gap is not observed in both compounds, which is consistent with the theoretical prediction.

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