Field-induced magnetic ordering in the Haldane system PbNi$_2$V$_2$O$_8$

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The Haldane system PbNi$_2$V$_2$O$_8$ was investigated by the temperature dependent magnetization $M(T)$ measurements at fields higher than $H_c$, with $H_c$ the critical fields necessary to close the Haldane gap. It is revealed that $M(T)$ for $H > H_c$ exhibits a cusplike minimum at $T_{\text{min}}$, below which $M(T)$ increases with decreasing $T$ having a convex curve. These features have been observed for both $H \parallel c$ and $H \perp c$, with $c$ axis being parallel to the chain. These data indicate the occurrence of field-induced magnetic ordering around $T_{\text{min}}$. Phase boundaries for $H \parallel c$ and $H \perp c$ do not cross each other, consistent with the theoretical calculation for negative single-ion anisotropy $D$.

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I. INTRODUCTION

Quantum spin systems with energy gaps have attracted considerable attention because of their rich variety of interesting phenomena. In these systems, the ground state is a nonmagnetic singlet state, and there exists a finite energy-gap between the ground and the excited magnetic states. Under certain magnetic fields $H_c$, the energy of one of the magnetic excited states becomes lower than that of the singlet state, where nonmagnetic-magnetic crossover occurs. Recently, special attention is paid to the magnetic transition that develops just above $H_c$. In these spin-gap systems, a number of novel phenomena is reported in these fields; for example, magnetic ordering of TiCuCl$_3$ in fields is interpreted as the Bose-Einstein condensation (BEC) of magnons. For the two dimensional dimer system SrCu$_2$(BO$_3$)$_2$, superlattice formation of localized triplet is observed.

The Haldane systems, i.e., quasi-one-dimensional Heisenberg antiferromagnets with integer spins, also are ones of the most extensively studied spin gap systems. For this class, unfortunately, field-induced magnetic ordering has hardly been observed experimentally. The archetypal Haldane-system, Ni(C$_2$H$_4$N$_2$)$_2$NO$_2$(ClO$_4$)$_2$ (NENP), shows no evidence of field-induced ordering down to 0.2 K in fields up to 13 T. Instead, the existence of an energy gap was revealed even at $H_c$. This is explained by the existence of a staggered field on Ni sites, which arises because the principal axis of the g tensor in NENP tilts alternately. This fact results in the slow crossover from nonmagnetic to magnetically polarized state in NENP, preventing from phase transition induced by fields.

So far, field-induced ordering in Haldane-systems was reported only for two cases: in Ni(C$_8$H$_{14}$N$_2$)$_2$N$_3$(PF$_6$) and Ni(C$_5$H$_{14}$N$_2$)$_2$N$_3$(ClO$_4$), abbreviated NDMAP and NDMAZ, respectively. Field-induced transitions in these systems were demonstrated by specific heat and neutron diffraction experiments. In the ordered state, interestingly, unusual spin excitations are observed. ESR and inelastic neutron-scattering experiments on NDMAP have revealed the existence of three distinct excitations in the ordered phase. This feature is quite different from those in a conventional Neel state, where dominant excitations are the spin-wave modes. Field-induced ordered phase in Haldane-systems is thus expected to illustrate much kind of novel physics, if much more examples are available.

Here the compound PbNi$_2$V$_2$O$_8$ would be another candidate for the Haldane system where field-induced ordering can be observed experimentally. PbNi$_2$V$_2$O$_8$ has a tetragonal crystal structure with Ni$^{2+}$ ($S = 1$) ions forming a chain along the c-axis. Magnetic susceptibility, high-field magnetization, and inelastic neutron scattering experiments were performed and their results consistently suggest that this system is a Haldane-gap system. The spin-gap closes at $H^\parallel = 14$ T and $H^\perp = 19$ T, where $H^\parallel$ and $H^\perp$ are the critical fields applied parallel and perpendicular to the chain (c-axis), respectively. These values of $H_c$ are within experimentally accessible range. Moreover, PbNi$_2$V$_2$O$_8$ is reported to exhibit impurity-induced magnetic transition around 3 K. This transition was found to be a long-range magnetic ordering by the neutron diffraction as well as the specific heat measurements. These facts suggest the relatively large interchain coupling, $J_1$. In fact, the $D - J_1$ plot (Sakai-Takahashi diagram) for this compound, where $D$ is the single-ion anisotropy, suggests that PbNi$_2$V$_2$O$_8$ is in the spin-liquid (disordered) regime but very close to the long-range ordered regime. Hence, one can expect that applying fields beyond $H_c$ will result in the magnetic ordering.

In the present paper, we have investigated magnetic properties of PbNi$_2$V$_2$O$_8$ at $H > H_c$ using temperature dependent measurements of magnetization in static fields up to 30 T, and have observed indication of magnetic ordering above $H_c$.

II. EXPERIMENTAL

Field-oriented powder sample of PbNi$_2$V$_2$O$_8$ was prepared as in the first report since single crystalline samples are not yet available. Powder sample of PbNi$_2$V$_2$O$_8$ was synthesized by a solid state reaction from PbO (99.999% pure), NiO (99.99%) and V$_2$O$_5$ (99.99%). They
were mixed and heated in air, firstly at 600°C and subsequently at 750°C for several days with intermittent grindings.

Powder X-ray diffraction (XRD) pattern agrees well with the calculated pattern based on the structure refined by the neutron diffraction experiments, and no second phase was detected. The powder was aligned by a magnetic fields (6 T) in stycast. The orientation was checked by the (004) XRD peak. The result confirmed that the c-axis aligns parallel to the magnetic fields, as is reported previously.19 In the following, we refer to magnetization measured under fields parallel to the c-axis, as $M^\parallel$, and to that under fields perpendicular to the c-axis, as $M^\perp$.

Magnetization was measured by an extraction method. Magnetic fields up to 15 T were generated by a superconducting magnet. Fields higher than 15 T were generated by a hybrid magnet at the Tsukuba Magnet Laboratory. For the measurements of magnetization as a function of magnetic fields, the fields were swept at the rate about 0.3 Tesla per minute at the temperature of 1.5 K. For the temperature-dependent measurements, magnetization was measured under constant magnetic fields.

III. RESULTS AND DISCUSSION

Fig.1 shows field dependence of the magnetization $M^\parallel(H)$ and $M^\perp(H)$ measured at $T = 1.5$ K. Both the $M^\parallel(H)$ and $M^\perp(H)$ curves steeply increase above the critical fields, $H_c^\parallel = 19$ T and $H_c^\perp = 13.5$ T, respectively. These values correspond to the critical fields at which the Haldane gap closes, and are in good agreement with the previous report obtained by the pulsed-field experiments.20

Here the $M(H)$ just above $H_c$ increases almost linearly with $H$. This behavior differs from the theoretical predictions, where $M(H)$ varies as proportional to $\sqrt{H - H_c}$ for axially symmetric fields ($H \parallel c$).24,25 One of the reason of this discrepancy can be the finite temperature effect. The $\sqrt{H - H_c}$ dependence easily becomes invisible by a slight thermal excitation, as is observed in NDMAZ.22 Other origins can be imperfect powder orientation, that can lead axially-asymmetric fields even for $H \parallel c$. However, it is also possible that the linear $M(H)$ is intrinsic behavior of an antiferromagnetically ordered system. When the measured temperature is sufficiently low compared to the energy gap, the system promptly enters the antiferromagnetically ordered regime above $H_c$, as is shown below.

Fig.2(a) shows temperature dependence of the magnetization measured under fields parallel to the c-axis, $M^\parallel(T)$. For $H < H_c^\parallel = 19$ T, the $M^\parallel(T)$ curves show no anomalies. Below 5 K, $M^\parallel(T)$ have small but finite values ($0.02 - 0.03\mu_B$), and these are attributed to the saturation magnetization of impurity and/or defects. For $H = 22$ T, there exists a cusp-like minimum at around $T_{\text{min}} = 6.4$ K. With increasing fields, $T_{\text{min}}$ shifts to higher temperatures systematically. $T_{\text{min}}$ reaches to 11.5 K at $H = 30$ T, as is seen in the figure.

Fig.2(b) shows temperature dependence of the magnetization measured under fields perpendicular to the c-axis, $M^\perp(T)$. Similar to the above results, $M^\perp(T)$ also exhibits a cusp-like minimum for $H > H_c^\perp = 13.5$ T. In this compound, it is demonstrated that $T_{\text{min}}$ at which $M(T)$ has a minimum is the Néel temperature, from the neutron diffraction26 and the specific heat measurements.27 Similarly, such cusp-like anomalies in $M(T)$ curves are shown to be the ordering temperature in the $S = 1/2$ alternating chain Pb$_2$V$_3$O$_8$ (ref.28) and the quasi-2-dimensional BaCuSi$_2$O$_6$ (ref.29) from specific heat measurements. We hence conclude that the data shown in Fig.2 also demonstrate the occurrence of field-induced magnetic ordering with Néel temperatures around $T_{\text{min}}$.

It is notable that the Haldane system NDMAP exhibits a minimum in $M(T)$ for $H > H_c$, at temperatures much higher than $T_N$.30 The origin of the minimum is not yet clear, and possibly related to a crossover into the low-temperature Tomonaga-Luttinger(TL) liquid regime, as is predicted for non-interacting one-dimensional ladders.31 A This is purely a one-dimensional phenomenon, and the three-dimensional ordering occurs at much lower temperatures.32 For those cases, $M(T)$ curves around $T_{\text{min}}$ are characterized by the relatively broad minimum and the concave curve.11,30,32 This is in clear contrast
with the cusp-like anomalies and the convex curve below $T_{\text{min}}$ in the present study as well as in those reported for TlCuCl$_3$ etc., which signals the 3-dimensional magnetic ordering. It is of course important to perform other experiments in order to verify the magnetic ordering at $T_{\text{min}}$. The lack of single crystalline samples makes it difficult to measure the specific heat of this anisotropic compound. We are then planning to measure the NMR spectra at high fields.

It may be interesting to compare the ordered-state induced by fields in PbNi$_2$V$_2$O$_8$ with that induced by impurity-doping in PbNi$_2$-$x$Mg$_x$V$_2$O$_8$. It is shown that the ordered-state of the latter has inhomogeneous distribution of magnetic moment, by ESR and $\mu$SR experiments. In addition, the impurity-induced ordered state vanishes at fields higher than $H = 4$ T, where the Haldane state with an energy gap recovers. In contrast, ordered state observed in the present experiments shows up only above $H_c$. The largest value of $T_{\text{min}}$ in the present study is $\sim 10$ K for $H = 30$ T, which is much larger than the maximum value of $T_N$ induced by Mg-doping, 3.3 K or the value of $zJ_1 \sim 0.03J \approx 3.1$K, with $z$ the number of nearest chains, and $J$ the intrachain coupling. This fact implies that the field-induced ordering occurs via the developed antiferromagnetic-correlation along the chain, and the ordered moment induced by fields is distributed uniformly on the chain.

In Fig.3, the values of $T_{\text{min}}$ are plotted against the applied fields. This corresponds to the magnetic phase diagram for PbNi$_2$V$_2$O$_8$. For both of $H \parallel c$ and $H \perp c$, $T_{\text{min}}$ increases with fields. It is notable that the phase boundaries for $H \parallel c$ and $H \perp c$ do not cross each other at least within the field range measured. This is in qualitative agreement with the theoretical calculation by Sakai the $HT$ phase diagram calculated for a Haldane chain with negative $D$. Indeed, $D/J = -0.05$ is estimated for PbNi$_2$V$_2$O$_8$ from inelastic neutron scattering experiments. In contrast, it is reported that crossing of the phase boundaries occurs in the phase diagram of NDMAP and NDMAZ and is well explained by the theoretical calculation for positive $D$. Thus, PbNi$_2$V$_2$O$_8$ is the first example of field-induced order in the Haldane system with negative $D$.

Since the early stage of the research of the Haldane systems, its magnetic state at $H > H_c$ has been discussed theoretically in terms of the BEC picture. In the following, we discuss on the possible condensed state in the ordered phase. In Fig.2 (a), one can see that $M^\parallel(T)$ increases below $T_{\text{min}}$ with decreasing $T$. Such increase cannot be explained by a conventional mean-field theory which predicts almost flat $M(T)$ below the ordered temperature. Instead, this increase is successfully explained by the magnon BEC theory, as to be due to the increase of magnon number as the condensation sets in.
It is rather surprising that the $M^\perp(T)$ also increases below $T_{\text{min}}$ as is seen in Fig.2(b). Here $H$ is applied perpendicularly to $D$, thereby the rotational symmetry of the Hamiltonian around $H$ is broken. In such cases, magnon BEC picture is not assured because the number of bosons is not conserved. In fact, the $M^\perp(T)$ of NDMAP does not increase below $T_N$ but becomes flat against $T$.

Such behavior is consistent with the Ising-like antiferromagnet that is predicted to develop for $H \perp D$. For the present system, the similarity of $M^\perp(T)$ and $M^\parallel(T)$ may be due to the relatively small $D$ ($D/J = -0.05$). This point should be studied more carefully.

It should be remarked, however, that the BEC picture requires some rigorous conditions. First, the concentration of magnons must be enough dilute. In fact, experiments on KCuCl$_3$, isostructural of TiCuCl$_3$, showed that the $M(T)$ curve becomes flat below $T_N$ for fields well above $H_c$. This behavior implies that for this dense magnon condition, mean field approximation is a better description. The BEC picture should hence be applied only for the region $H - H_c \sim 0$. Moreover, it is recently argued that some anisotropic interactions arising from spin-orbit coupling like the Dzyaloshinsky-Moriya(DM) interaction and/or the staggered $g$ effect can be qualitatively modify the BEC description, even if the interactions are very weak. Recent ESR measurements on TiCuCl$_3$ have indeed suggested the existence of such interactions. For the present case, the screw-like crystal structure of PbNi$_2$V$_2$O$_8$ may cause the DM interaction, as is suggested to explain the weak-ferromagnetism in the isostructural SrNi$_2$V$_2$O$_8$.

IV. CONCLUSIONS

We have observed cusp-like anomaly at $T_{\text{min}}$ in the $M(T)$ curves for $H > H_c$. The value of $T_{\text{min}}$ increases with applied fields. These observations suggest the evolution of field-induced magnetic ordering in the Haldane chain system PbNi$_2$V$_2$O$_8$. Magnetic phase diagram of this system up to 30 T is presented. The phase boundaries for $H \parallel c$ and $H \perp c$ do not cross each other, in qualitative agreement with the $HT$ phase diagram calculated theoretically for a Haldane system with $D < 0$.

In the ordered phase, it is revealed that the magnetizations increase with decreasing $T$ and the $M(T)$ have a convex curve for both the directions $H \parallel c$ and $H \perp c$. These features may support that the magnon Bose-Einstein condensation picture can be applicable as an approximation for Haldane gap systems at least for $H \parallel c$. However, possible anisotropic effects including the Dzyaloshinsky-Moriya interaction can modify the description of the ordered state significantly.

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