Field-induced magnetic ordering in the Haldane system $PbNi_2V_2O_8$

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The Haldane system $PbNi_2V_2O_8$ was investigated by temperature-dependent magnetization $M(T)$ measurements at fields higher than H_c; H_c is the critical field required to close the Haldane gap. It has been revealed that for $H>H_c$, $M(T)$ exhibits a cusplike minimum at T_{min}, below which it increases with a decrease in T following a convex curve. These results were observed for both $H\|c$ and $H\perp c$, with the c axis parallel to the chain. These data indicate the occurrence of field-induced magnetic ordering around T_{min}. The phase boundaries for $H\|c$ and $H\perp c$ do not cross each other. This result is consistent with the theoretical calculation for a negative single-ion anisotropy D.

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I. INTRODUCTION

Quantum spin systems with energy gaps have attracted considerable attention because they exhibit various interesting phenomena. In these systems, the ground state is a nonmagnetic singlet state, and there exists a finite energy-gap between the ground and 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, at which a nonmagnetic-magnetic crossover occurs. Recently, special attention has been paid to the magnetic transition that occurs just above H_c in these spin-gap systems.[1] A number of phenomena have been reported in these fields. For example, the magnetic ordering of $TlCuCl_3$ in magnetic fields is interpreted as the Bose-Einstein condensation (BEC) of magnons.[2,3] A superlattice formation of localized triplets has been observed for the two-dimensional dimer system $SrCu_2(BO_3)_2$.[4]

The Haldane systems, i.e., quasi-one-dimensional Heisenberg antiferromagnets with integer spins, are also one of the most extensively studied spin-gap systems. However, field-induced magnetic ordering for this class has rarely been observed experimentally. The archetype Haldane system, $Ni(C_2H_8N_2)_2NO_2(ClO_4)$ (NENP),[5] shows no evidence of field-induced ordering down to 0.2 K in fields up to 13 T.[6] Instead, the existence of an energy gap was revealed even at H_c.[6] This result can be explained by the presence of a staggered field at Ni sites, which is produced by the alternate tilting of the principal axis of the g tensor in NENP.[7,8] Therefore, slow crossover from a nonmagnetic to a magnetically polarized state occurs in NENP, thereby preventing phase transition induced by the fields.

Thus far, field-induced ordering in Haldane systems has been reported only for two cases: $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ and $Ni(C_5H_{14}N_2)_2N_3(ClO_4)$, abbreviated as NDMAP and NDMAZ, respectively. The field-induced transitions in these systems were demonstrated by specific heat[9–12] and neutron diffraction experiments.[13,14] Interestingly, unusual spin excitations are observed in the ordered state. Electron spin resonance[15] (ESR) and inelastic neutron-scattering experiments[16] on NDMAP have revealed the existence of three distinct excitations in the ordered phase. This feature is rather different from that in the conventional Néel state, in which the spin-wave modes are the dominant excitations.[17] Thus, field-induced ordered state in Haldane systems can have potential implications for physics, if more examples were available.

The compound $PbNi_2V_2O_8$ would be another candidate for the Haldane system in which field-induced ordering can be observed experimentally. $PbNi_2V_2O_8$ has a tetragonal crystal structure wherein Ni^{2+} ($S=1$) ions form 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.[18] The spin gap closes at $H_c^{\|}=14$ T and $H_c^{\perp}=19$ T,[18] where $H_c^{\|}$ and $H_c^{\perp}$ are the critical fields applied parallel and perpendicular to the chain (c axis), respectively. These H_c values are within the experimental range. Moreover, $PbNi_2V_2O_8$ is reported to exhibit an impurity-induced magnetic transition around 3 K.[18] This transition was found to be that of the long-range antiferromagnetic ordering by neutron powder diffraction[19] and specific heat measurements.[20] These results suggest the relatively large interchain coupling, J_1. In fact, the D-J_1 plot[21] (Sakai-Takahashi diagram) for this compound, where D is the single-ion anisotropy, indicates that although $PbNi_2V_2O_8$ is in the spin-liquid (disordered) regime, it is very close to the long-range ordered regime.[22] Hence, the application of fields beyond H_c will result in the magnetic ordering. In the present paper, we have investigated the magnetic properties of $PbNi_2V_2O_8$ at $H>H_c$ by temperature-dependent measurements of magnetization in static fields up to 30 T, and have observed magnetic ordering above H_c.

II. EXPERIMENT

A field-oriented powder sample of $PbNi_2V_2O_8$ was prepared as shown in the first report,[18] since single crystalline samples are not yet available. It was synthesized from PbO (99.999% pure), NiO (99.99%), and V_2O_5 (99.99%) by a solid state reaction. They were mixed and heated in air, first at 600 °C and then at 750 °C for several days with intermittent grindings.

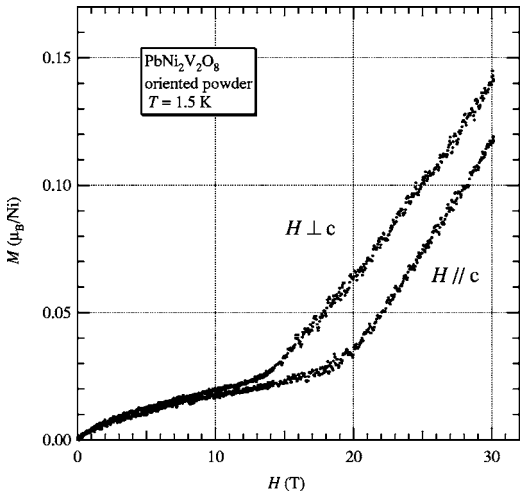

FIG. 1. Field dependence of the magnetization of the $PbNi_2V_2O_8$ powder samples.

The powder x-ray diffraction (XRD) pattern was in good agreement with the calculated pattern based on the structure refined by the neutron diffraction experiments,[19,23] and no second phase was detected. The powder was aligned by a magnetic field (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 field, as reported previously.[18] Hereafter, we refer to the magnetization measured under fields parallel to the *c* axis as $M^{\parallel}$, and 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 measurements of magnetization as a function of magnetic fields, the fields were swept at the rate about 0.3 T/min at 1.5 K. For temperature-dependent measurements, magnetization was measured at constant magnetic fields.

III. RESULTS AND DISCUSSION

Figure 1 shows the field dependence of the magnetizations $M^{\parallel}(H)$ 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 those of the previous report obtained by pulsed-field experiments.[18]

In the figure, $M(H)$ increases almost linearly with H just above H_c. This behavior differs from that predicted theoretically, where $M(H)$ varies in proportion to $\sqrt{H-H_c}$ for axially symmetric fields ($H\|c$).[24,25] One of the reasons for this discrepancy can be the finite temperature effect. The $\sqrt{H-H_c}$ dependence easily disappears by a small thermal excitation, as observed in NDMAZ.[12] Other contributing factors could be the imperfect powder-orientation, that can generate axially asymmetric fields even for $H\|c$. However, it is also possible that the linear $M(H)$ is an intrinsic characteristic of an antiferromagnetically ordered system. When the measured temperature is sufficiently low as compared with the energy gap, the system immediately enters the antiferromagnetic ordered regime above H_c, as shown below.

Figure 2(a) shows the temperature dependence of 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, the values of $M^{\parallel}(T)$ are small but finite (0.02–$0.03\mu_B$). They are attributed to the saturation magnetization of impurities and/or defects. For $H=22$ T, there exists a cusplike minimum at around $T_{min}=6.4$ K. With increasing fields, T_{min} shifts to higher temperatures systematically. It reaches 11.5 K at $H=30$ T, as shown in the figure.

Figure 2(b) shows the temperature dependence of magnetization measured under fields perpendicular to the *c* axis, $M^{\perp}(T)$. Similar to the above results, $M^{\perp}(T)$ also exhibits a cusplike minimum for $H>H_c^{\perp}=13.5$ T.

In both Figs. 2(a) and 2(b), the slope of $M(T)$ sharply changes at T_{min}. Moreover, below T_{min}, $M(T)$ increases with a decrease of T following a convex curve, as shown clearly

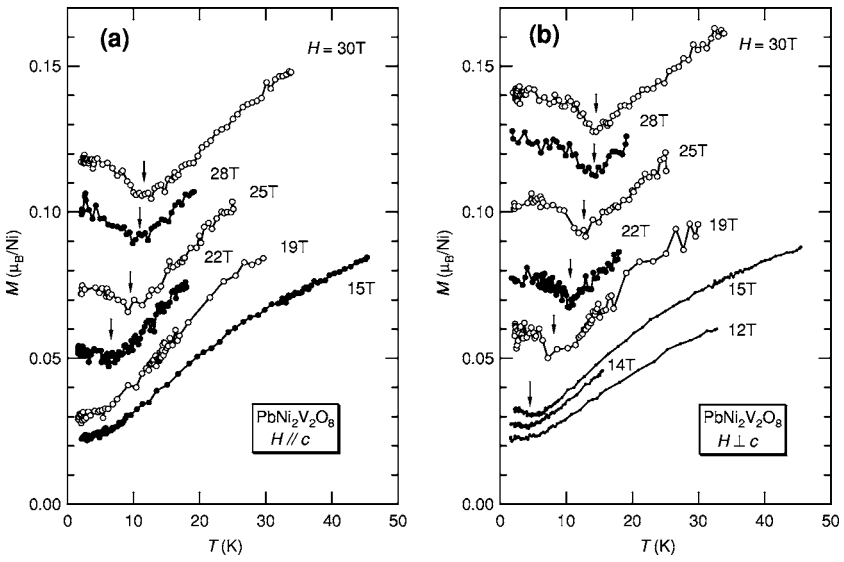

FIG. 2. Temperature dependence of the magnetization of $PbNi_2V_2O_8$ for (a) $H\|c$ and (b) $H\perp c$. Arrows indicate T_{min} described in the text.

in the curve of $M^{\perp}(T)$ at $H=30$ T [Fig. 2(b)]. Such $M(T)$ curves closely resemble the field-induced magnetic ordering of the coupled-dimer compound $TlCuCl_3$.[2,3] For this compound, T_{min} at which $M(T)$ is minimum is shown to be the Néel temperature, by means of the neutron diffraction[26] and specific heat measurements.[27] Similarly, based on the specific heat measurements, such cusplike anomalies in the $M(T)$ curves are shown to be the ordering temperature for the $S=1/2$ alternating chain $Pb_2V_3O_9$ (Ref. 28) and the quasi-two-dimensional $BaCuSi_2O_6$.[29] Hence, we conclude that the data shown in Fig. 2 also indicate the occurrence of field-induced magnetic ordering with Néel temperatures around T_{min}.

It should be noted that $M(T)$ of the Haldane system NDMAP has a minimum for $H>H_c$ at temperatures much higher than T_N.[11,30] The origin of the minimum has not yet been clarified, and possibly related to a crossover into the low-temperature Tomonaga-Luttinger (TL) liquid regime, as predicted for noninteracting one-dimensional ladders.[31,32] This is purely a one-dimensional phenomenon, and the three-dimensional ordering occurs at much lower temperatures.[32] In such cases, the $M(T)$ curves around T_{min} are characterized by a relatively broad minimum and a concave curve.[11,30,32] This is in clear contrast to the cusplike anomalies and convex curve below T_{min} in the present study as well as in those reported for $TlCuCl_3$, which indicates three-dimensional magnetic ordering. It is evidently important to perform other experiments in order for verifying the magnetic ordering at T_{min}. Due to a lack of single crystalline samples, it is difficult to measure the specific heat of this anisotropic compound. Therefore, we plan to measure the nuclear magnetic resonance (NMR) spectra at high fields.

It may be interesting to compare the ordered state induced by the fields in $PbNi_2V_2O_8$ with that induced by the impurity doping in $PbNi_{2-x}Mg_xV_2O_8$.[18] ESR (Ref. 33) and μSR experiments[19] have revealed that the ordered state of the latter has an inhomogeneous distribution of magnetic moment. In addition, the impurity-induced ordered state, which depends on the amount of the Mg dopants, disappears progressively at fields as high as $H=4$ T, where the Haldane state with an energy gap recovers.[19,20] In contrast, the ordered state observed in the present experiments appears only above H_c. The largest value of T_{min} in the present study is ~ 10 K for $H=30$ T, which is considerably larger than the maximum value of T_N induced by Mg doping, 3.3 K,[33] or the value of $zJ_1 \sim 0.03J \simeq 3.1$ K, where z is the number of nearest chains, and J is the intrachain coupling.[22] This result implies that the field-induced ordering occurs through the developed antiferromagnetic correlation along the chain, and the ordered moment induced by the fields is distributed uniformly along the chain.

In Fig. 3, the values of T_{min} are plotted against the applied fields. This plot corresponds to the magnetic phase diagram for $PbNi_2V_2O_8$. For both $H \| c$ and $H \perp c$, T_{min} increases with the fields. It should be noted that the phase boundaries for $H \| c$ and $H \perp c$ do not cross each other at least within the measured field range. This result is in qualitative agreement with the theoretical calculation by Sakai;[34] the HT phase diagram for a Haldane chain with a negative D. In fact, $D/J=-0.05$ is estimated for $PbNi_2V_2O_8$ from inelastic neutron scattering experiments.[22] In contrast, it has been reported that the phase boundaries in the phase diagram of NDMAP and NDMAZ cross each other,[10,12] which is explained in detail by the theoretical calculation for a positive D.[35] Thus, $PbNi_2V_2O_8$ is the first example of field-induced ordering in the Haldane system for a negative D.

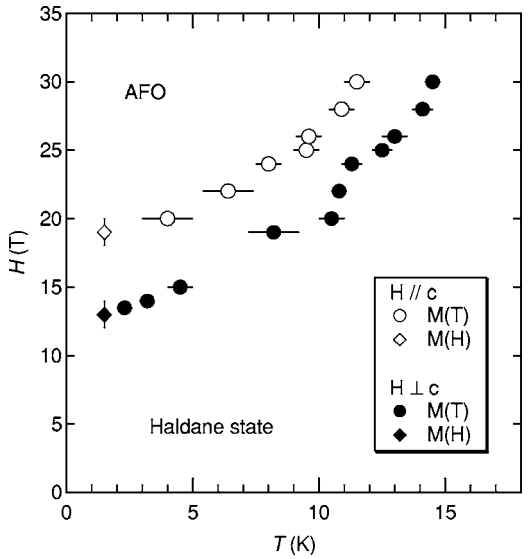

FIG. 3. Magnetic phase diagram of $PbNi_2V_2O_8$ derived from the present experiments (symbols). "AFO" and "Haldane state" represent the antiferromagnetically ordered state and the nonmagnetic spin-singlet state with a Haldane gap, respectively. Open symbols represent the data for $H \| c$, while filled ones are for $H \perp c$. Circles indicate T_{min} determined from the $M(T)$ curves, while diamonds indicate H_c estimated from the $M(H)$ curves.

Since the initial research of the Haldane systems, their magnetic state at $H>H_c$ has been discussed theoretically in terms of the BEC picture.[24,36] We discuss the possible condensed state in the ordered phase in the following. In Fig. 2(a), $M^{\|}(T)$ remarkably increases below T_{min} with a decrease of T. Such an increase cannot be explained by the conventional meanfield theory,[37] which predicts an almost flat $M(T)$ below the ordering temperature. On the other hand, the magnon BEC theory successfully explains that the increase is due to the increase in the magnon number as the condensation occurs.[2] For applying the magnon BEC theory to our case, it is essential that the rotational symmetry around the magnetic field be conserved.[2] In the present case, the rotational symmetry would be conserved for $M^{\|}(T)$.

Surprisingly, $M^{\perp}(T)$ also increases below T_{min} as shown in Fig. 2(b). In this case, H is applied perpendicularly to D, thereby the rotational symmetry of the Hamiltonian around H is broken. In such cases, the magnon BEC picture would not be valid because the number of bosons is not conserved.[2] In fact, $M^{\perp}(T)$ of NDMAP does not increase below T_N but flattens against T.[11,30] This behavior is consistent with that of the Ising-like antiferromagnet, which is predicted to occur for $H \perp D$.[35] In the present system, the similarity between $M^{\perp}(T)$ and $M^{\|}(T)$ may be due to the relatively small D $(D/J=-0.05)$. This point should be studied in greater detail.

It should be remarked, however, that the BEC picture requires some rigorous conditions be satisfied. First, the con-

centration of magnons must be sufficiently dilute.[2] In fact, experiments on $KCuCl_3$, the isostructural of $TlCuCl_3$, showed that the $M(T)$ curve becomes flat below T_N for fields much greater than H_c.[38] This behavior implies that for this dense magnon condition, the mean-field approximation is an appropriate description. Hence, the BEC picture should be applied only to the region $H-H_C \sim 0$. Moreover, it was recently argued that some anisotropic interactions originating from spin-orbit coupling, such as the Dzyaloshinsky-Moriya interaction and/or the staggered g effect, can qualitatively modify the BEC description, even if they are very weak.[39,40] Recent ESR measurements of $TlCuCl_3$ have suggested the existence of such interactions.[41] In the present case, the screwlike crystal structure of $PbNi_2V_2O_8$ may result in these anisotropic interactions.

IV. CONCLUSIONS

We have observed the cusplike anomaly at T_{min} in the $M(T)$ curves for $H > H_c$. The value of T_{min} increases with applied fields. These observations suggest the evolution of the field-induced magnetic ordering in the Haldane chain system $PbNi_2V_2O_8$. The magnetic phase diagram of this system up to 30 T is presented. The phase boundaries for $H \| c$ and $H \perp c$ do not cross each other. This diagram qualitatively agrees with the HT phase diagram that was calculated theoretically for a Haldane system with $D < 0$.[34]

In the ordered phase, it is revealed that the magnetizations increase with a decrease of T and $M(T)$ has a convex curve for both directions $H \| c$ 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 $H \| c$. However, possible anisotropic effects such as the Dzyaloshinsky-Moriya interaction can significantly modify the description of the ordered state.

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