Spin-Vacancy-Induced Long-Range Order in a New Haldane-Gap Antiferromagnet

Y. Uchiyama,1 Y. Sasago,1 I. Tsukada,1 K. Uchinokura,1,2,* A. Zheludev,3 T. Hayashi,4 N. Miura,4 and P. Bön5

1Department of Applied Physics, The University of Tokyo, 6th Eng. Bld., Bunkyo-ku, Tokyo 113-8656, Japan
2Department of Advanced Materials Science, The University of Tokyo, 6th Eng. Bld., Bunkyo-ku, Tokyo 113-8656, Japan
3Physics Department, Brookhaven National Laboratory, Upton, NY 11973-5000, U.S.A.
4Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8666, Japan
5Laboratory for Neutron Scattering ETH & PSI, CH-5232, Villigen PSI, Switzerland

(Received 12 April, 1999)

Magnetic susceptibility, high-field magnetization and inelastic neutron scattering experiments are used to study the magnetic properties of a new $S = 1$ quasi-1-dimensional antiferromagnet PbNi$_2$V$_2$O$_4$. Inter-chain interactions are shown to be almost, but not quite, strong enough to destroy the nonmagnetic singlet ground state and the energy gap in the magnetic excitation spectrum. Substituting nonmagnetic Mg$^{2+}$ ($S = 0$) ions for Ni$^{2+}$ ($S = 1$) induces a magnetically ordered state at low temperatures. To our knowledge this is the first observation of doping-induced long-range order in a Haldane-gap system.

PACS numbers: 75.30.Kz, 75.30.Hx, 75.40.Cx, 75.40.Gb

Unlike its classical counterpart, the quantum Heisenberg antiferromagnet (HAF) has a nonmagnetic spin-singlet ground state in one-dimensional (1D) space. A pioneering work by Haldane \[1\] led to a breakthrough in our understanding of this remarkable phenomenon, and of low-dimensional magnetism in general. Haldane suggested that the actual ground states are totally different for integer- and half-integer-spin systems. The half-integer 1D HAF shows quasi-long-range order (power-law spin correlations). True long-range order can be induced by the slightest perturbations. In contrast, for integer spins the ground state singlet is robust. Intrachain spin correlations decay exponentially (true short-range order) and the excitation spectrum has a nonzero energy gap. The system remains nonmagnetic even in the presence of weak magnetic anisotropy or residual 3-dimensional (3D) interactions. The spectacular properties of the integer-spin quantum HAF have been extensively studied theoretically and experimentally, and are by now rather well understood. The current issue in quantum magnetism is how the singlet ground state is finally destroyed and long-range order (LRO) is formed when perturbations to the idealized Hamiltonian become sufficiently strong.

Among the factors that favor an ordered ground state are single-ion anisotropy and 3D interchain coupling in quasi-1D HAF systems. Increasing either of these parameters beyond some critical level leads to a quantum phase transition to a state with a Néel-like order parameter. This effect has been extensively studied and the corresponding phase diagram is known from numerical simulations \[2\]. As anticipated by Shender and Kivelson \[3\], another potential source of magnetic LRO is the introduction of spin-vacancies in the quantum chains. Indeed, replacing some of the $S = 1$ ions by $S = 0$ sites severs the chains and liberates $S = 1/2$ end-chain degrees of freedom \[4\]. Under certain circumstances these free spins can order in 3D space. To date however this phenomenon has not been observed in any material, and is poorly understood theoretically. In the present paper we report the first observation of spin-vacancy-induced ordering in a new Haldane-gap compound PbNi$_2$V$_2$O$_4$, that sports a peculiar helical arrangement of magnetic ions and substantial (yet subcritical) interchain interactions.

The exact crystal structure of PbNi$_2$V$_2$O$_4$ has not been reported yet \[5\]. Preliminary X-ray diffraction measurements on powder samples prepared by conventional solid-state reaction suggest that this material is isomorphous with SrNi$_2$V$_2$O$_8$ \[6\] (Fig. 1, inset). SrNi$_2$V$_2$O$_8$ is tetragonal (space group $I_{4}d$) with lattice parameters $a = 12.1617$ Å and $c = 8.3247$ Å. We found that PbNi$_2$V$_2$O$_4$ has the same crystal symmetry and very similar lattice parameters: $a = 12.249(3)$ Å and $c = 8.354(2)$ Å. In the two isostructural compounds slightly distorted NiO$_6$ octahedra are edge-shared around the four-fold screw axis along the $c$ direction. All the $S = 1$ Ni$^{2+}$ ions, as well as all the nearest neighbor (NN) Ni$^{2+}$-Ni$^{2+}$ bonds are equivalent. The screw-chains are separated by VO$_4$ tetrahedra and Sr$^{2+}$ or Pb$^{2+}$ ions. Intrachain nearest-neighbor Ni-Ni antiferromagnetic interactions are expected to dominate. The V$^{5+}$ sites are presumed nonmagnetic.

To characterize the new Pb-based system, bulk magnetic measurements were performed on highly aligned polycrystalline samples. These were prepared by applying a magnetic field of 9 T at room temperature to a mixture of PbNi$_2$V$_2$O$_4$ powder and epoxy resin (Stycast

*E-mail:uchinokura@ap.t.u-tokyo.ac.jp
The Ni-chains tend to align themselves along the applied magnetic field. A c-axis alignment of better than 3° (FWHM) was achieved, as determined from measuring the rocking curve of the 004 Bragg reflection. Magnetic susceptibility was measured with a commercial SQUID magnetometer. The experimental \( \chi(T) \) curves, shown in Fig. 2, have a broad maximum around 120 K for both \( H \perp c \) and \( H \parallel c \). Below this temperature, \( \chi(T) \) decreases exponentially to almost zero. The residual low-\( T \) susceptibility can be attributed to the presence of paramagnetic impurities. A straightforward analysis of the data collected in the range \( 0 < T < 40 \) K yields the thermal activation energies: \( \Delta = 29.4 \) K = 2.53 meV for \( H \parallel c \), and \( \Delta = 27.8 \) K = 2.39 meV for a transverse field, respectively. In addition to the susceptibility measurements, high-field magnetization data were taken on an aligned polycrystalline sample in magnetic fields of up to 40 T, using the pulsed magnetic facility at ISSP. Figure 3 shows magnetization curves measured at \( T = 4.2 \) K. At high fields an abrupt change of slope in \( M(H) \) is observed for both \( H \parallel c \) and \( H \perp c \). The corresponding critical fields are \( H_c(\perp) = 14 \) T and \( H_c(\parallel) = 19 \) T.

![Figure 1](https://via.placeholder.com/150)

**FIG. 1.** Temperature dependence of magnetic susceptibility measured in PbNi\(_2\)V\(_2\)O\(_8\). The solid line shows data for a nonaligned powder sample. The symbols are for highly aligned polycrystalline samples. The magnitudes of data for aligned samples are not exact because we cannot exactly estimate the quantity of the powder contained in the resin. True magnitude for \( H \parallel c \) should be larger than that for \( H \perp c \) because of the c-axis alignment. Inset: A schematic view of the crystal structure of (Sr/Pb)Ni\(_2\)V\(_2\)O\(_8\).

The activated temperature dependence of magnetic susceptibility is a clear signature of a nonmagnetic ground state. The distinct chain-arrangement of magnetic \( S = 1 \) Ni\(_{2}^{+}\) ions in the crystal structure suggests that we are in fact dealing with a Haldane antiferromagnet. The behaviour of high-field magnetization is also typical of a Haldane-gap system [3]. The starting point for describing the magnetism of PbNi\(_2\)V\(_2\)O\(_8\) should therefore be a nearest-neighbor Heisenberg Hamiltonian with a possible uniaxial single-ion anisotropy (tetragonal crystal structure!): \( H = J \sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1} + D \sum_i (S_i^z)^2 \). For not too large \( D \) the ground state is a Haldane singlet. The lowest energy excitations are a single longitudinal mode and a doublet of transverse-polarized Haldane excitations. Using Eq. (2.14) in Ref. [8], relating the critical fields \( H_c(\perp) \) and \( H_c(\parallel) \) to the doublet and singlet gap energies \( \Delta_\perp \) and \( \Delta_\parallel \), we obtain \( \Delta_\perp = 2.2 \) meV and \( \Delta_\parallel = 1.2 \) meV. The intrachain exchange constant \( J \) can be deduced from the high-temperature part of the measured \( \chi(T) \) curves [8]. For PbNi\(_2\)V\(_2\)O\(_8\), this analysis yields \( J = 95 \) K = 8.2 meV. Already we see that the mean gap energy \( (2\Delta_\perp + \Delta_\parallel)/3 = 1.87 \) meV is substantially smaller that the value \( 0.41J \approx 3.36 \) meV, expected for noninteracting chains [8]. The most likely source of this discrepancy is substantial interchain exchange interactions. In their presence the excitation energies become dependent on the momentum transfer perpendicular to the chain axis. \( \Delta_\perp \) and \( \Delta_\parallel \) in this case represent the global minima in the 3D dispersion, and cannot be uniquely related to \( J \).

Dynamic spin correlations in PbNi\(_2\)V\(_2\)O\(_8\) were studied in a series of inelastic neutron scattering experiment on a 10 g powder sample at the D"r"u"ch"aL 3-axis spectrometer (SINQ spallation source, PSI, Switzerland). Neutrons of fixed final energy \( E_f = 8 \) meV were used with a (guide)-80°-80°-(open) collimation setup. An entire series of constant-\( E \) scans was collected in the energy range 2-8 meV to map out the low-energy part of the magnetic dynamic structure factor \( S(Q,\omega) \). Additional data were collected in constant-\( Q \) scans. A typical data set measured at a momentum transfer just exceeding the 1D antiferromagnetic zone-center \( Q_c = 4\pi/c \) at \( T = 2 \) K is.

![Figure 2](https://via.placeholder.com/150)

**FIG. 2.** Magnetization curves measured in PbNi\(_2\)V\(_2\)O\(_8\) at \( T = 4.2 \) K for magnetic fields parallel and perpendicular to the chain axis.
shown in the inset in Fig. 3. This and all other const-Q scans clearly show the presence of a spin gap of roughly 3.5 meV. The main panel in Fig. 3 shows a constant-E scan measured at $\hbar \omega = 4$ meV, i.e., just above the gap energy. In order to analyze these data we have calculated the powder average of the 3D dynamic magnetic structure factor for an isolated screw-shaped Haldane chain, as appropriate for PbNi$_2$V$_2$O$_8$ [10]. The relevant parameters of this cross section are the two gap energies $\Delta_\perp$ and $\Delta_\parallel$. Although this model (dashed lines in Fig. 3) can reproduce the measured const-Q scans fairly well and predicts the asymmetric feature at $Q_\pi$, it cannot account for the sharp peak seen at $Q \approx 3\pi/c$ in constant-E scans.

A better agreement with the experiment could only be obtained by taking into account interchain interactions. We assumed a weak Heisenberg coupling between nearest-neighbor Ni chains and treated it on the RPA level. A detailed description of this analysis is beyond the scope of this Letter, and will be published elsewhere [10]. Compared to the noninteracting-chain model only one additional parameter, namely the interchain coupling constant $J_\perp$ is introduced. The total number of variables is minimized by fixing the lowest excitation energies to the gap values deduced from high-field measurements. An excellent global fit to the data is obtained with $J_\perp = 0.096 \pm 0.003$ meV from least squares refinement (solid lines in Fig. 3). From this value and the measured critical fields the intrinsic gap energies for noninteracting chains can be determined: $\Delta_\perp^{(0)} = 4.1$ meV and $\Delta_\parallel^{(0)} = 3.7$ meV, respectively. Using the numerical results from Ref. [8], for the intrachain coupling constant $J$ and the anisotropy parameter $D$ we obtain $J = 9.5$ meV and $D = -0.23$ meV (easy-axis), respectively. The former value is in reasonably good agreement with the high-$T$ susceptibility estimate $J = 8.2$ meV.

The results presented above enable us to place the new material on the Sakai-Takahashi $D - J_\perp$ phase diagram [2]. For PbNi$_2$V$_2$O$_8$ we have $D/J \approx -0.024$, $J_\perp/J = 0.01$ and $z = 4$, $z$ being the coordination number for interchain interactions. Using Fig. 8 in Ref. [2], we find that PbNi$_2$V$_2$O$_8$ is positioned in the Haldane phase, just below the borderline with the ordered Ising-like phase. In other words, by shear chance the system is almost critical towards the formation of long-range order. As will be reported elsewhere [11], unlike PbNi$_2$V$_2$O$_8$, the isostructural SrNi$_2$V$_2$O$_8$ system falls on the opposite side of the transition line and actually ordered in 3D space in a weak-ferromagnetic structure below $T_N = 7$ K. A simple substitution of nonmagnetic Sr for nonmagnetic Pb slightly alters the coupling geometry, increasing interchain interactions or single-ion anisotropy beyond the critical values.

Having characterized the pure PbNi$_2$V$_2$O$_8$ compound, we now turn to the main subject of this paper, describing the emergence of Néel-like magnetic LRO upon introduction of spin vacancies in this Haldane-gap system. Nonmagnetic sites are introduced into the spin chains by substituting $S = 0$ Mg$^{2+}$ ions for the $S = 1$ Ni$^{2+}$. The measured temperature dependences of magnetic susceptibility for a series of Pb(Ni$_{1-x}$Mg$_x$)$_2$V$_2$O$_8$ powder samples with $x$ ranging from 0 to 0.120 are shown in Fig. 4. Except for the $x = 0$ compound, an increase of susceptibility is observed at low $T$ in all samples studied. The enhancement scales with Mg concentration, and can be attributed to the presence of free $S = 1/2$ spins at the ends of the Ni chains severed by the spin vacancies [12]. In this scenario the number of liberated spins is twice the number of substitutions. To check this scaling we compared the temperature dependence of magnetic susceptibility in Mg$^{2+}(S = 0)$- and Cu$^{2+}(S = 1/2)$-substituted PbNi$_2$V$_2$O$_8$. The replacement of a Ni$^{2+}$ ion by a Cu$^{2+}$ ion also produces two end-chain spins. However, these two spins couple antiferromagnetically to the Cu-spin, producing a ground state configuration of total $S = 1/2$. The total number of added free spins in this case is equal to the total number of added $S = 1/2$ ions. Experimentally, the measured $\chi(T)$ curve for 2%-Cu-doped PbNi$_2$V$_2$O$_8$ sample was found to be virtually indistinguishable from that for a 1%-Mg-doped sample.

The central result of this work is the observation of a sharp decrease in the magnetic susceptibility of Pb(Ni$_{1-x}$Mg$_x$)$_2$V$_2$O$_8$ below $T_c \approx 3.5$ K for $x \geq 0.20$. The slope of $\chi(T)$ changes abruptly with reversing its sign. This behavior is a clear indication of a magnetic phase transition. Its nature is revealed in experiments on an aligned powder sample with $x = 0.030$ (Inset of Fig. 3). In this case the transition point is about $T_c = 3.0$ K. Below this temperature a large anisotropy of susceptibility is observed. For $H \parallel c$, $\chi(T)$ decreases abruptly below $T_c$. In contrast, for $H \perp c$ it remains...
practically constant. This behavior is typical of a Néel antiferromagnet with spins ordering along the c direction, that, as we have shown previously, is the magnetic easy axis of the system.

The effect of spin-vacancy substitution has been studied experimentally (see, for example, Ref. [12] and theoretically [4]) for a number of Haldane-gap systems. Apart from the appearance of free end-chain spins and the resulting paramagnetic contribution to the low-T susceptibility, severing the chains leads to a reduction of the dynamic spin correlation length. PbNi$_2$V$_2$O$_8$ is, to our knowledge, the first example of a Haldane AF that orders magnetically upon doping. The key of course is in the interchain interactions: to order magnetically the liberated end-chain spins need to be coupled in 3D space. As we have demonstrated, interchain coupling is quite substantial in PbNi$_2$V$_2$O$_8$. The possibility of vacancy-induced LRO in a Haldane-gap system was first qualitatively discussed by Shender and Kivelson [3]. In particular, the authors suggested that there is a critical impurity concentration below which LRO does not occur. As to this point more detailed low-T studies are required.

![FIG. 4. Temperature dependences of magnetic susceptibility measured in Pb(Ni$_{1-x}$Mg$_x$)$_2$V$_2$O$_8$ (0 ≤ x ≤ 0.120) powder samples. The inset shows the data for a highly aligned Pb(Ni$_{0.97}$Mg$_{0.03}$)$_2$V$_2$O$_8$.](image)

The magnetic transition that we observe in Pb(Ni$_{1-x}$Mg$_x$)$_2$V$_2$O$_8$ should not be confused with that in the extensively studied Haldane system CsNiCl$_3$ [13,14]. Unlike in PbNi$_2$V$_2$O$_8$, direct interchain interactions in CsNiCl$_3$ are stronger than the critical value, and even the undoped material has a magnetically ordered ground state. In fact, the introduction of Mg$^{2+}$ vacancies leads to a decrease of the ordering temperature [15], in striking contrast with the behavior of PbNi$_2$V$_2$O$_8$. Rather, the situation in Mg-doped PbNi$_2$V$_2$O$_8$ is similar to that in the spin-Peierls CuGeO$_3$, doped with Zn [16], Mg [17] or Ni [18], and the two-leg ladder system SrCu$_2$O$_3$ doped with Zn. Although these materials are half-integer-spin antiferromagnets, their ground states fall in the same universality class as the Haldane state, and they both have a gapped magnetic excitation spectrum. Just as we propose for PbNi$_2$V$_2$O$_8$, the onset of long-range order is believed to be caused by interchain interactions that couple free spins liberated by impurity substitution. Doping-induced long-range magnetic order thus appears to be a universal feature of quasi-1D singlet quantum antiferromagnets with the excitation gap.

In summary, we have shown that PbNi$_2$V$_2$O$_8$ is a Haldane-gap system with substantial interchain interactions and is almost critical towards the formation of long-range order. For the first time long-range magnetic ordering was induced in a Haldane antiferromagnet by spin-vacancy substitution on the $S = 1$ sites.

We would like to thank T. Masuda for the cooperation in the various aspects of this work. This work was supported in part by Grant-in-Aid for COE Research “Phase Control of Spin-Charge-Photon (SCP) Coupled System” from the Ministry of Education, Science, Sports, and Culture. Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886, Division of Material Science, U.S. Department of Energy.

[1] F. D. M. Haldane, Phys. Lett. A93, 464 (1983); Phys. Rev. Lett. 50, 1153 (1983).
[2] T. Sakai and M. Takahashi, Phys. Rev. B 42, 4537 (1990).
[3] E. F. Shender and S. A. Kivelson, Phys. Rev. Lett. 66, 2384 (1991).
[4] J. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, Phys. Rev. Lett. 59, 899 (1987); Commun. Math. Phys. 115, 477 (1988).
[5] B. Wanklyn, J. Mater. Sci. 13, 89 (1978).
[6] R. Wichmann and Hk. Müller-Buschbaum, Rev. Chim. Miner. 23, 1 (1986).
[7] K. Katsumata et al., Phys. Rev. Lett 63, 86 (1989); Z. Honda, H. Asakawa, and K. Katsumata, Phys. Rev. Lett. 81, 2566 (1998).
[8] O. Golinelli, Th. Jolicœur, and R. Lacaze, J. Phys.: Cond. Matt. 5, 7847 (1993).
[9] V. Gadet et al., Phys. Rev. B 44, 705 (1991).
[10] A. Zheludev et al., to be published.
[11] Y. Uchiyama et al., to be published.
[12] M. Hagiwara et al., Phys. Rev. Lett. 65, 3181 (1990).
[13] W. J. L. Buyers et al., Phys. Rev. Lett. 56, 4 (1986); Phys. Rev. B 38, 543 (1988).
[14] K. Kakurai et al., J. Phys. (Paris) Colloq. 49, C8-1433 (1988).
[15] S. S. Sosin et al., JETP 85, 114 (1997).
[16] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. 70, 3651 (1993); M. Hase et al., Phys. Rev. Lett.
[17] T. Masuda et al., Phys. Rev. Lett. 80, 4566 (1998).

[18] N. Koide et al., cond-mat/9805051 (1998).

[19] M. Azuma et al., Phys. Rev. B 55, R8658 (1997).