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Field-induced long-range order in the $S=1$ antiferromagnetic chain

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The quasi-one-dimensional $S=1$ antiferromagnet in magnetic field H is investigated with the exact diagonalization of finite chains and the mean-field approximation for the interchain interaction. In the presence of the single-ion anisotropy D, the full phase diagram in the HT plane is presented for $H\parallel D$ and $H\perp D$. The shape of the field-induced long-range ordered phase is revealed to be quite different between the two cases, as observed in the recent experiment of $Ni(C_5H_{14}N_2)_2N_3(PF_6)$ (NDMAP). The estimated ratio of the interchain and intrachain couplings of NDMAP ($J'/J \sim 10^{-3}$) is consistent with the neutron-scattering measurement.

Since Haldane conjectured[1] the presence of the spin excitation gap in the one-dimensional integer-S Heisenberg antiferromagnets, the $S=1$ antiferromagnetic chain has attracted a lot of interest. Many theoretical and numerical works indicated the disordered ground state of the system. The mean-field approximation for the interchain interaction combined with the exact diagonalization of finite chains[2] revealed that such a disordered ground state should be realized even in the quasi-one-dimensional $S=1$ antiferromagnet if the ratio of the interchain and intrachain couplings holds $zJ'/J \lesssim 0.05$ where z is the number of adjacent chains. It was derived from the value of the staggered susceptibility of a single chain in the ground state ($\chi_{\mathrm{st\,(1D)}} \sim 20/J$).[3,4] The criterion was satisfied for the material $Ni(C_2H_8N_2)_2NO_2(ClO_4)$,[5] abbreviated NENP. In fact the Haldane gap had already been observed in the temperature dependence of the magnetic susceptibility[5] and the high-field magnetization measurements of NENP.[6,7]

The effective-field theory[8] and the size scaling analysis with the finite chain calculation[9,10] indicated that the field-induced transition occurs from the disordered ground state to the gapless Tomonaga-Luttinger liquid phase at some critical external field H_{c1} where the Haldane gap vanishes. With the interchain interaction, the gapless phase would become the ordered phase. Thus the field-induced antiferromagnetic long-range order is expected to appear at H_{c1} in the quasi-one-dimensional $S=1$ system. NENP, however, did not exhibit such a field-induced spontaneous symmetry breaking, because the staggered moment is forced to appear even by a smaller external field through the alternation of the g tensors.[11–13] Recently the field-induced transition to the long-range order was discovered in the high-field magnetization measurement of quasi-one-dimensional $S=1$ systems $Ni(C_5H_{14}N_2)_2N_3(ClO_4)$ (Ref. 14) and $Ni(C_5H_{14}N_2)_2N_3(PF_6)$,[15] abbreviated NDMAZ and NDMAP, respectively. The magnetic susceptibility measurement indicated the presence of the easy-plane single-ion anisotropy D for both systems and the value was reported as $D \sim 0.3J$ for NDMAP. The experimental phase diagram of both systems in the HT plane exhibited a quite different shape of the ordered phase between the two cases when the external field H is (a) parallel and (b) perpendicular to the principal axis of D. This is probably because the universality of the symmetry breaking is different between the two cases. Thus it would be interesting to present the theoretical HT phase diagram. In this paper, using the exact diagonalization of finite chains and the mean-field approximation for the interchain interaction, the phase diagrams for $H\parallel D$ and $H\perp D$ are presented to compare with the experimental ones and give some suggestions for future experiments.

In order to investigate the magnetization process of the quasi-one-dimensional $S=1$ antiferromagnet with the planar single-ion anisotropy, we consider the Hamiltonian,

$$\mathcal{H} = J\sum_j \sum_i \mathbf{S}_{j,i}\cdot\mathbf{S}_{j,i+1} + J'\sum_{\langle j,j'\rangle}\sum_i \mathbf{S}_{j,i}\cdot\mathbf{S}_{j',i} + D\sum_j\sum_i (S^z_{j,i})^2 - H\sum_j\sum_i S^\alpha_{j,i}, \tag{1}$$

where J and J' are the intrachain and interchain couplings, respectively, j is the index of a chain, and $\Sigma_{\langle j,j'\rangle}$ means the sum over all the pairs of nearest-neighbor chains. We set $J=1$ and use the units such as $g\mu_B=1$ throughout the paper. Only the XY-like anisotropy $D>0$ is investigated, to compare with the experimental results of NDMAP. To consider the two cases (a) $H\parallel D$ and (b) $H\perp D$, we set $\alpha=z$ and y, respectively. When the antiferromagnetic order is possibly induced by the external field H, the xy plane is an easy plane for (a) while the x axis is an easy axis for (b). Thus the universality class of the symmetry breaking should be different between the two cases; the former corresponds to the XY model $[U(1)]$ while the latter the Ising one (Z_2).

In the magnetization process at low temperatures two phase transitions are expected to occur at critical fields $H_{c1}(T)$ and $H_{c2}(T)$. At $T=0$ the Haldane gap vanishes at $H_{c1}(0)$ and the magnetization is saturated at $H_{c2}(0)$. The antiferromagnetic long-range order in the vertical direction to H should appear between $H_{c1}(T)$ and $H_{c2}(T)$. Based on the mean-field approximation for the interchain interaction, the critical field $H_{c1}(T)$, as well as $H_{c2}(T)$ is determined by the solution H of the equation

$$\chi^\rho_{\mathrm{st\,(1D)}}(T,H) = \frac{1}{zJ'}, \tag{2}$$

where $\chi^\rho_{\mathrm{st\,(1D)}}(T,H)$ is the staggered susceptibility of the one-dimensional system ($J'=0$) and ρ ($=x$, y, or z) specifies the easy component of the antiferromagnetic order. To

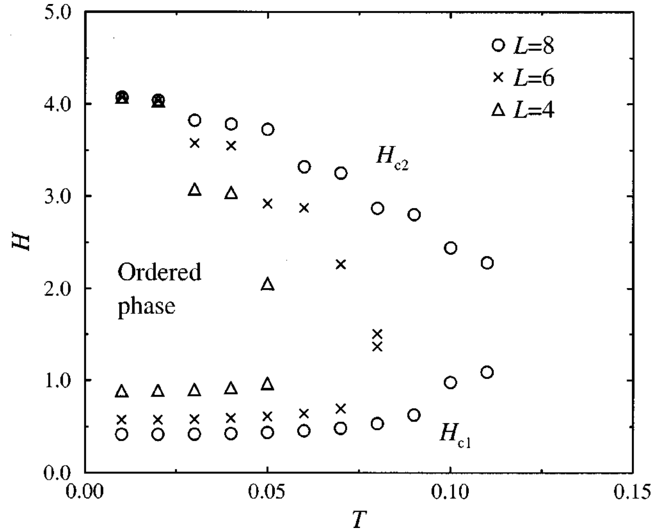

FIG. 1. $H_{c1}(T)$ and $H_{c2}(T)$ plotted versus T for $L=8$, 6, and 4. The finite-size effect is revealed to underestimate the ordered phase.

consider the two cases (a) and (b) we set $(\alpha,\rho)=(z,x)$ and (y,x), respectively. Using the numerical diagonalization analysis, we obtain all the eigenvalues and eigenvectors of finite chains and calculate $\chi^{\rho}_{\mathrm{st\,(1D)}}(T,H)$. Since the rotational symmetry does not remain in any direction for $H\perp D$, the available chain length is at most $L=8$ under the periodic boundary condition because of limitation of the memory size. At finite temperature, however, the correlation length is much smaller than that at $T=0$ ($\xi\sim5$ to 6 lattice constants for $H=D=0$). Thus even the result for $L=8$ is expected to indicate some qualitative features of the bulk system. In fact the small oscillation in the H dependence of $\chi^{\rho}_{\mathrm{st\,(1D)}}(T,H)$ due to the finite-size effect only appears at $T\lesssim0.1$ for $L=8$. Since $\chi^{\rho}_{\mathrm{st\,(1D)}}(T,0)$ monotonously decreases with increasing T like the Curie-Weiss law at high temperatures, the two field-induced transitions at H_{c1} and H_{c2} can occur at suitable temperatures as far as $\chi^{\rho}_{\mathrm{st\,(1D)}}(T,H)$ has a maximum as a function of H. The present calculation for $D=0$ indicated that $\chi^{\rho}_{\mathrm{st\,(1D)}}(T,H)$ has such a maximum for $T\lesssim1$ while it is a monotonously decreasing function of H for $T\gtrsim1$, almost independently of L. The amplitude of $\chi^{\rho}_{\mathrm{st\,(1D)}}(1,0)$ is about 2. Thus the criterion of the existence of the two field-induced transitions should be $zJ'\lesssim0.5$ in the isotropic case. For $zJ'\gtrsim0.5$ only one transition from the Néel to disordered states occurs at H_{c2} for $T\lesssim1$ while no transition occurs for $T\gtrsim1$. In the present analysis we concentrate on the case of $zJ'\lesssim0.5$. Based on obtained $H_{c1}(T)$ and $H_{c2}(T)$ from the calculation for $L=8$, we discuss the properties of the phase diagram in the HT plane in the following.

To investigate the finite-size effect, we show in Fig. 1 $H_{c1}(T)$ and $H_{c2}(T)$ of the isotropic system ($D=0$) with $zJ'=0.05$ determined by Eq. (2) for $L=8$, 6, and 4 in the HT plane. The lower and upper boundaries of the antiferromagnetic ordered phase are given by $H_{c1}(T)$ and $H_{c2}(T)$, respectively. Those lines also give the H dependence of the Néel temperature T_{N}. Figure 1 indicates that estimated T_{N} is higher for larger L, which suggests that the finite-chain analysis tends to underestimate the ordered phase. On the other hand, the mean-field approximation generally overestimates it. Thus in the present analysis the finite-size effect and the fluctuation around the mean field are expected to suppress the errors due to each other.

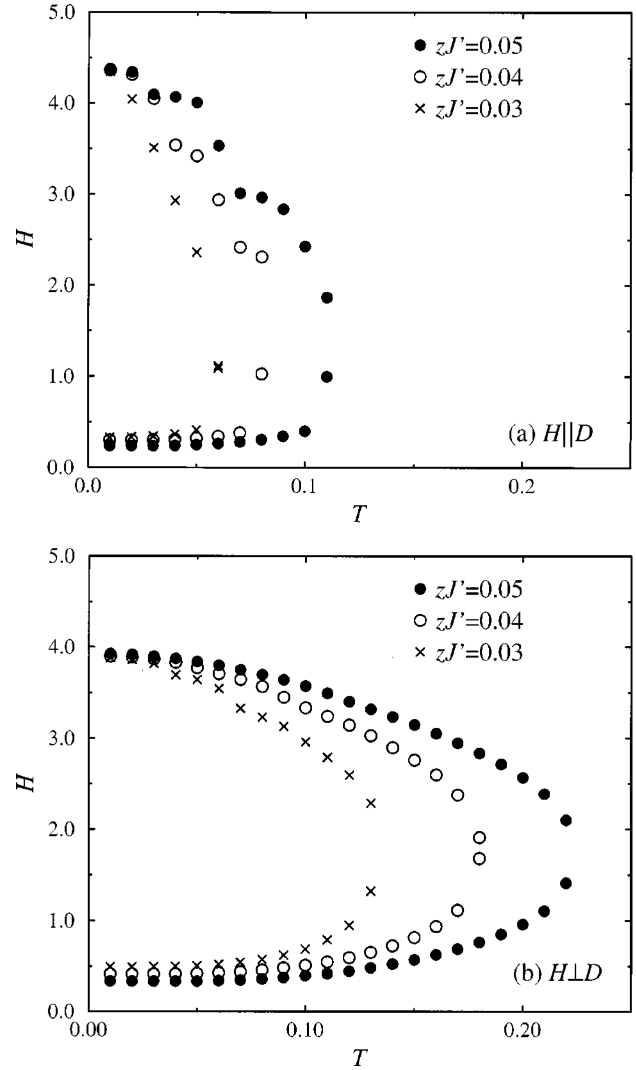

FIG. 2. Phase diagrams in the HT plane for (a) $H\|D$ and (b) $H\perp D$ with $D=0.3$.

In the following analysis we put $D=0.3$, realistic for NDMAP. The phase diagrams in the HT plane obtained from $\chi^{\rho}_{\mathrm{st\,(1D)}}(T,H)$ for $L=8$ are shown in Figs. 2(a) and 2(b), for $H\|D$ and $H\perp D$, respectively. The phase boundaries for $zJ'=0.05$, 0.04, and 0.03 are given in each case. Although $H_{c2}(T)$ exhibits an oscillation due to finite-size effect, Fig. 2(a) clarifies an interesting feature; $H_{c1}(T)$ and $H_{c2}(T)$ are quite asymmetric for $H\|D$. In contrast, H dependence of T_{N} is close to a symmetric bell shape for $H\perp D$. According to our calculation for other values of D, the difference in the shape of T_{N} becomes clearer for larger D. With increasing D, T_{N} becomes more asymmetric for $H\|D$, while closer to a completely symmetric bell shape for $H\perp D$. The asymmetric behavior of T_{N} for $H\|D$ is consistent with the H dependence of the critical exponent η in the transverse spin-correlation function $\langle S^x_0 S^x_r\rangle\sim(-1)^r r^{-\eta}$ of the isotropic $S=1$ chain at $T=0$. In the ground-state magnetization process of the system the antiferromagnetic spin correlation measured by η rapidly grows from H_{c1} to the maximum while it slowly decays toward H_{c2}. Thus such an asymmetric behavior is

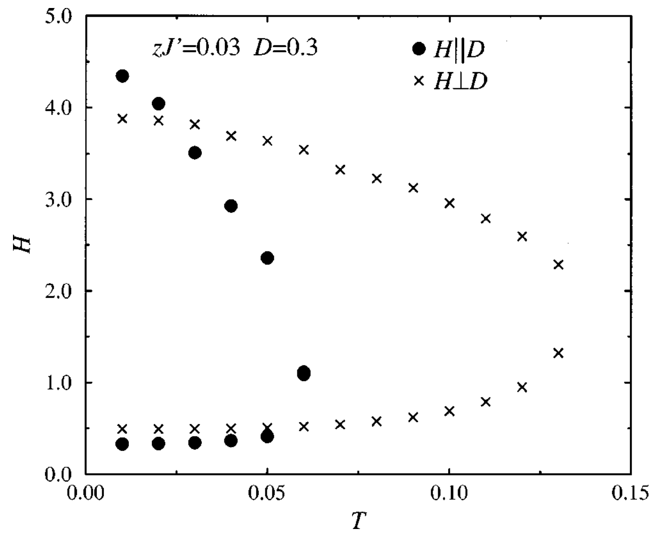

FIG. 3. Phase diagrams for $H \| D$ and $H \perp D$ with $zJ' = 0.03$ and $D = 0.3$.

expected to be characteristic of the system with $U(1)$ symmetry. On the other hand, the case (b) with only Z_2 symmetry is supposed to be close to a classical spin system where the spin-wave excitation spectrum around $m \sim 1$ is similar to that around $m \sim 0$.

The phase diagrams for $H \| D$ and $H \perp D$ ($zJ' = 0.03$) are shown together in Fig. 3. They exhibit several characteristic behaviors observed in the experiments of NDMAP and NDMAZ: (i) At lower temperatures $H_{c1}(T)$ is smaller for $H \| D$. (ii) At intermediate H T_N is higher for $H \perp D$. (iii) The two T_N curves have two intersections, although the upper one has not been observed because such a strong magnetic field cannot be realized. (i) and (ii) imply that the ordered state resulting from the $U(1)$ (Z_2) symmetry breaking is less (more) sensitive to the external magnetic field, while less (more) stable against the thermal fluctuation. Our calculation for various values of D indicates that the intersection of two T_N curves appears only for $D > 0$. Thus the observed intersection is also an evidence of the positive D for NDMAP and NDMAZ. It is consistent with the sign of D determined by the susceptibility measurements.[15,14] The feature (i) at $T = 0$ is also explained by the Majorana-fermion representation of the $S = 1$ antiferromagnetic chain,[16] which was justified by the NMR experiment[17] NENP. When the angle θ between H and D varies from 0 to $\pi/2$, $H_{c1}(0)$ continuously increases from m_1 to $\sqrt{m_1 m_2}$ in the fermion picture where m_1 and m_2 are the masses of the two different fermions ($m_1 < m_2$). From the viewpoint of the present universality argument, it is expected that some superpositions of the $U(1)$ and Z_2 symmetry breaks occur at $H_{c1}(T)$ for an intermediate angle θ. Since the ratio of the two components [$U(1)$ and Z_2] continuously varies depending on θ, $H_{c1}(T)$ should be a continuous function of θ, as the fermion theory suggested.

The qualitative consistency of the present results with the experiments of NDMAP encourages us to estimate the strength of the interchain coupling J' of NDMAP by fitting the calculated phase boundaries to the measured one. The calculated phase boundaries [$H_{c1}(T)$ and $H_{c2}(T)$] for $zJ' = 0.010$, 0.012, and 0.014 are shown together with the experimental results of NDMAP in Figs. 4(a) $H \| D$ and 4(b) $H \perp D$, where dashed curves are guides for the eyes. We set $D = 0.3$. The temperature is normalized as $J = 30$ K and the magnetic field is normalized such that $H_{c1}(0)$ coincides with the experimental results. In Fig. 4(a) it is difficult to fit the calculated T_N curve to the experimental one, because there appear some plateaulike behaviors which reflect level crosses in the ground-state magnetization process of finite systems. Thus we determine zJ' by the agreement of the maximum value of T_N as $zJ' = 0.012 \pm 0.002$. On the other hand, the fit of the calculated T_N to the measured one is much better for $H \perp D$ in Fig. 4(b). It leads to the same conclusion $zJ' = 0.012 \pm 0.002$. However, the error of the estimation might be much larger, because we neglect the finite-size correction and the fluctuation around the mean field of the interchain couplings. Since the number of the adjacent chains is usually more than 2, the result $zJ'/J \sim 0.012$ leads to $J'/J \sim 10^{-3}$. It is consistent with the most dominant interchain coupling estimated from the recent neutron-scattering experiment.[18] Using the same mean-field approximation with the transfer matrix calculation of the chain, a little smaller value of zJ'/J

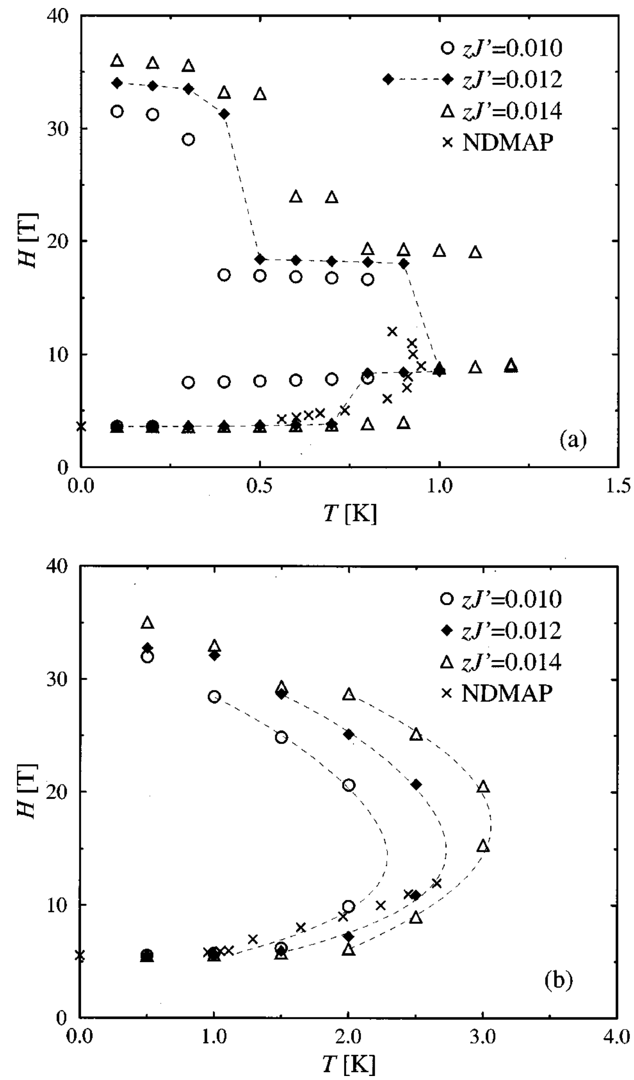

FIG. 4. Calculated phase diagrams for $zJ' = 0.010$, 0.012 and 0.014, shown with the experimental results of NDMAP, in the cases of (a) $H \| c$ axis and (b) $H \perp c$ axis. Dashed curves are guides for the eyes.

was estimated.[19] It is a reasonable difference, because the size correction of the present analysis would shift the result to a smaller value. However, it is difficult to determine which result is better, because some analyses beyond the mean-field approximation should modify it into a larger value. Figure 4(b) suggests that the maximum of T_N of NDMAP could be detected with a little larger external field even for $H\perp D$. It would also enable us to perform a more precise estimation of J' and confirm the difference in the shape of T_N between $H\|D$ and $H\perp D$.

Recently a sign of the field-induced long-range order was also observed in the NMR measurement[20] of another quasi-one-dimensional $S=1$ system $(CH_3)_4NNi(NO_2)_3$, abbreviated TMNIN. Since J is smaller ($J\sim 12$ K), the full magnetization curve has already been obtained.[21] Thus the full phase diagram in the HT plane will possibly be determined in the near future. It would clarify more detailed features of the field-induced long-range order.

In summary, based on the mean-field approximation for the interchain interaction and numerical diagonalization of finite chains, we obtained the phase diagram in the HT plane of the quasi-one-dimensional $S=1$ antiferromagnet. The results revealed that the shape of the field-induced ordered phase is quite different between $H\|D$ and $H\perp D$. Fitting the calculated phase boundary to the experimental result led to the estimation of the interchain coupling of NDMAP as $zJ'/J\sim 0.012$, which well agrees with the estimation by the recent neutron-scattering measurement ($J'/J\sim 10^{-3}$).

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