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Experimental realization of Lieb-Mattis plateau in a quantum spin chain

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Topological properties in material science have recently received tremendous attention, as exemplified by topological insulators. As for quantum spin systems, the Haldane chain with integer spins is the best known example¹. The realization of a topological quantum phase in the Haldane chain is an innovative research development related to the 2016 Nobel Prize in Physics. For mixed spin chains composed of two different spins, the appearance of a topologically quantized magnetization plateau is predicted by the Lieb-Mattis theorem² in combination with the Oshikawa-Yamanaka-Affleck criterion³. However, the actual magnetization plateau in the mixed spin chain has not yet been observed. Here, we present a model compound forming a mixed spin-(1/2, 5/2) chain. We observe a clear Lieb-Mattis plateau and well explain it quantitatively. The present results demonstrate a quantum many-body effect based on quantum topology and provide a new stage in the search for topological properties in condensed matter physics.

The one-dimensional (1D) spin chain is the simplest quantum spin model in which spins are linearly arranged. Variations of spin size and coupling in 1D spin chains cause a variety of quantum many-body phenomena through strong quantum fluctuations. Haldane's conjecture in 1983 came as a great surprise to the condensed matter physics community. He predicted that 1D spin chains would have fundamentally different properties depending on the value of the spins¹. Subsequent experimental and theoretical research has demonstrated that the Heisenberg antiferromagnetic (AF) chain with integer spins has an energy gap between the nonmagnetic ground state and the first excited state, whereas that with half-integer spins has no energy gap. The topological ground state of the Haldane chain can be described by a valence-bond picture², where each integer spin is considered as a collection of $S = 1/2$ and forms a singlet state between $S = 1/2$ spins on the different sites.

Mixed spin chains with antiferromagnetically coupled alternating $S = 1/2$ and $S > 1/2$ have attracted much attention as a research field for examining topological properties in quantum spin systems. The Lieb-Mattis (LM) theorem explains that the ground state of the mixed spin-(1/2, S) Heisenberg chain is a ferrimagnet with a value of $S - 1/2$ ³. Furthermore, the topological argument by the Oshikawa-Yamanaka-Affleck criterion⁴ predicts the appearance of a quantized magnetization plateau at $(S - 1/2)/(S + 1/2)$. Therefore, the mixed spin-(1/2, 5/2) chain, which we present in this work, is expected to exhibit a 2/3 magnetization plateau^{5,6}. A particular feature of the LM ferrimagnet is the presence of gapless ferromagnetic and gapped AF spin-wave excitations^{6–10}. The AF gap disappears when a magnetic field applied, and a quantum phase transition to the Luttinger-liquid (LL) phase is expected to appear corresponding to the end of the magnetization plateau and accompanied by a singular square root behavior of the magnetization^{5,6,11}.

From an experimental perspective, several candidates for mixed spin-(1/2, S) Heisenberg chains have been reported more than 20 years ago. Bimetallic coordination compounds with 3d transition metals are typical examples^{12–17}. Further, several molecular materials composed of organic radical and Mn^{2+} ion are expected to form mixed spin-(1/2, 5/2) chains^{18,19}. Although several compounds forming the mixed spin chain show a tendency towards a magnetization plateau, those behaviors are not distinguishable from the thermal paramagnetic state and do not provide conclusive evidence for the LM plateau associated with an energy gap^{12,14,17}. Considering the

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Figure 1. Crystal structure and mixed spin chain of (4-Br-*o*-MePy-V)FeCl₄. **(a)** Molecular structures of (4-Br-*o*-MePy-V)FeCl₄. **(b)** Crystal structure forming a 1D chain along the *c* axis. Hydrogen atoms are omitted for clarity. The broken lines indicate two types of N-Cl short contact associated with *J* and *J'*. **(c)** Mixed spin-(1/2, 5/2) chain composed of *s* = 1/2 on the radical and *S* = 5/2 on the FeCl₄ anion through *J* and *J'*.

strong AF couplings in the candidate compounds, it is difficult to observe the entire predicted LM plateau using actual high-field measurements.

In this study, we realize a new mixed spin-(1/2, 5/2) chain in a charge-transfer salt (4-Br-*o*-MePy-V)FeCl₄ [4-Br-*o*-MePy-V = 3-(5-Br-1-methylpyridinium-2-yl)-1,5-diphenylverdazyl], and its molecular structure is shown in Fig. 1a. The verdazyl radical 4-Br-*o*-MePy-V and the FeCl₄ anion have spin-1/2 and 5/2, respectively. The crystallographic parameters are as follows: monoclinic, space group *P*21/*c*, *a* = 7.676(7) Å, *b* = 19.425(15) Å, *c* = 16.028(13) Å, β = 94.962(16)°, *V* = 2381(3) Å³, *Z* = 4, *R* = 0.0451, and *R*_w = 0.0994. The 4-Br-*o*-MePy-V and FeCl₄ form a 1D structure along the *c* axis, as shown in Fig. 1b. There are two types of short contacts between the N atom in the central verdazyl ring and the Cl atom, which are 4.04 Å and 3.80 Å, respectively. *Ab initio* molecular orbital (MO) calculations were performed in order to evaluate the corresponding exchange interactions between the spins on 4-Br-*o*-MePy-V and FeCl₄ molecules. They are evaluated as $J/k_B = 3.9$ K and $J'/k_B = 3.3$ K, which are defined in the Heisenberg spin Hamiltonian given by $H = J \sum_i \mathbf{s}_{2i-1} \cdot \mathbf{s}_{2i} + J' \sum_i \mathbf{s}_{2i} \cdot \mathbf{s}_{2i+1}$, where *s* and *S* are the spin-1/2 and 5/2 operators, respectively. The *J* and *J'* have very close values and form a mixed spin-(1/2, 5/2) chain with a slight alternation (*J'/J* = 0.85), as shown in Fig. 1c. We note that intermolecular interactions between organic radical and 3*d* transition metal anions tend to be underestimated. From our previous study²⁰, the actual values in verdazyl-based salts are expected to be approximately three times larger than those of the MO evaluation, i.e., $J/k_B \approx 12$ K and $J'/k_B \approx 10$ K. The MO calculations also indicated two types of interchain interactions (see Supplementary Information). However, the effective interchain couplings are sufficiently small to be ignored in the current discussion of the mixed spin chain, as described in the following analysis of magnetization.

Results and Discussion

Figure 2a shows the magnetization curve at 1.5 K. We observe a clear 2/3 magnetization plateau between approximately 2 and 30 T and subsequent gapless behavior. The magnetization curve reaches its saturation at approximately 40 T. Considering the isotropic *g* value of ~2.0 resulting from radical and Fe³⁺ ion in this compound, the saturation value of 5.7 μ_B/f.u. indicates that the purity of the radicals and anions is approximately 95%. We consider this purity in the following analysis. The field derivative of the magnetization curve (*dM/dB*) exhibits a double peak structure accompanied by a phase transition towards the gapless LL phase.

Here, we discuss the ground state of the present mixed spin-(1/2, 5/2) chain. We consider the uniform (*J* = *J'*) and alternating (*J* > *J'*) types. The uniform type is a typical model forming the LM ferrimagnet. Its ground state has the total spin *S*_{tot} = 2 per unit cell, which are degenerate at zero-field. The degeneracy is lifted by the finite magnetic field, and the eigenstate with *S*_{tot}^{*z*} = 2 becomes the lowest in the plateau region, as described in Fig. 2b. The LM theorem is also applied to the alternating type, and thus the ground state is expected to become a similar ferrimagnetic state with *S*_{tot}^{*z*} = 2. We can understand the situation by the valence bond picture in Fig. 2b, where the two spin-1/2 particles on the different sites form a nonmagnetic singlet dimer through *J*. We calculated the magnetization curves of the mixed spin-(1/2, 5/2) chain using the quantum Monte Carlo (QMC) method. The calculated result for the uniform type is confirmed to be the same as that of the previous works^{5,6}, and is shown in Fig. 2a. We obtained good agreement between the experiment and calculation by using $J/k_B = 9.0$ K. The calculated result reproduces not only the 2/3 magnetization plateau but also the field-induced LL phase. Further, the calculated *dM/dB* reproduces the double peak structure qualitatively. The slight differences in the low-field thermal paramagnetic²¹ and LL phases are considered to originate from the interchain interactions. Below the plateau phase, the effective spin-2 state fully polarizes at only approximately 2 T, which indicates the interchain couplings are much weaker than the intrachain ones. These weak interchain couplings are understood by the valence bond picture of the alternating type in Fig. 2b. The MO calculations indicate that the dominate interchain interactions are between *s* = 1/2 radicals (see Supplementary Information). However, the *s* = 1/2 spins can be regarded as forming a nonmagnetic singlet dimer. The effective interactions between the remaining spins are caused through the triplet excited states of the singlet dimers and become much weaker than the MO evaluations^{22–24}.

Figure 2. Magnetization curve of (4-Br-o-MePy-V)FeCl₄ and related valence bond pictures. **(a)** Magnetization curve of (4-Br-o-MePy-V)FeCl₄ at 1.5 K. The inset shows the field derivative of the magnetization curve (dM/dB). The broken lines represent the calculated results for the mixed spin-(1/2, 5/2) chain ($J = J'$, $\alpha = 1$) using the QMC method. **(b)** Valence bond pictures for the LM plateau on the two types of mixed spin-(1/2, 5/2) chain, i.e., uniform ($J = J'$) and alternating ($J > J'$) types. $S = 5/2$ spins are described by five $s = 1/2$ spins. The ovals represent valence bond singlet pairs of two $s = 1/2$ spins, $\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$.

Figure 3. Calculated magnetization curve of the mixed spin-(1/2, 5/2) chain with various values of $\alpha = J'/J$. Calculated magnetization curves **(a)** and their field derivative **(b)** at 1.5 K for the mixed spin-(1/2, 5/2) chain with various values of α by using QMC method. The magnetic field range extends the gapless region where the α dependence is relatively remarkable.

We examined the $\alpha = J'/J$ dependence of the magnetization curve. Figure 3a,b show the magnetization curve and dM/dB in the vicinity of the gapless phase for representative values of α , respectively. The value of J was determined for each α , so as to reproduce the central magnetic field in the gapless phase. Hence, the following values were obtained: $J/k_B = 9.0$ K ($\alpha = 1.0$), $J/k_B = 10.6$ K ($\alpha = 0.7$), $J/k_B = 11.9$ K ($\alpha = 0.5$), and $J/k_B = 13.5$ K ($\alpha = 0.3$). The magnetization curve increases relatively rapidly as the α decreases. The corresponding differences appear in dM/dB , where the shape of the peak dramatically changes with decreasing α . The decrease of α corresponds to a reduction of one-dimensionality towards a complete dimer without an intermediate LL phase for $\alpha = 0$. We confirm that the uniform type for $\alpha = 1$ is closest to the experimental result, and the α dependence becomes almost indistinguishable for $0.7 < \alpha < 1$. Accordingly, the actual value of α in the present model is considered to be between 0.7 and 1, which is consistent with the MO evaluation.

Figure 4a shows the temperature dependence of the magnetic susceptibility ($\chi = M/H$) at 0.1 T. We observe an anomalous change at 5.0 K, which indicates that a phase transition to the long-range order (LRO) occurs at $T_N = 5.0$ K owing to the small but finite interchain interactions. In the higher-temperature region, the value of χT exhibits a rounded minimum at approximately 24 K, as shown in the inset of Fig. 4a. This behavior is a typical characteristic of mixed spin chains^{13–16}. We then calculated χT for the uniform mixed spin-(1/2, 5/2) chain with $J/k_B = 9.0$ K by using the QMC method, obtaining a good agreement in the temperature region above T_N . The difference below T_N originates from the interchain interactions causing the AF LRO as in the case of the low-field part of the magnetization curve.

The experimental result for the specific heat at zero-field clearly exhibits a λ -type sharp peak associated with the phase transition to the LRO, which is consistent with the discontinuous change in the magnetic susceptibility, as

Figure 4. Magnetic susceptibility and specific heat of (4-Br-*o*-MePy-V)FeCl₄. **(a)** Temperature dependence of magnetic susceptibility ($\chi = M/H$) at 0.1 T. The arrow indicates the phase transition temperature T_N . The inset shows the temperature dependence of χT , where the position of the rounded minimum is marked with $T_{\min}$. The solid line with open squares represents calculated result for the mixed spin-(1/2, 5/2) chain ($J = J'$, $\alpha = 1$) by using QMC method. **(b)** Temperature dependence of the specific heat at various magnetic fields. The arrows indicate the phase transition temperatures T_N . For clarity, the values for 0.5, 1.0, 1.5, and 2.0 T have been shifted up by 8.6, 16, 22, and 27 J mol⁻¹ K, respectively.

shown in Fig. 4b. We have not observed the expected double peak and $\sqrt{T}$ behavior in the low-temperature region⁶ due to the phase transition behavior. Because the experimental behavior below T_N exhibits almost T -linear dependence, the gapless ferromagnetic dispersion is considered to change to an AF linear dispersion owing to the effect of the AF interchain interactions. In magnetic fields, the phase transition temperature decreases with increasing fields and almost disappears above 2 T, which is consistent with the formation of the plateau phase with a spin gap.

Conclusion

In conclusion, we have succeeded in synthesizing a new model compound forming a mixed spin-(1/2, 5/2) chain. We observe the entire magnetization curve up to saturation, which exhibits a clear Lieb-Mattis magnetization plateau and subsequent quantum phase transition towards the gapless LL phase. The present results demonstrate a quantum many-body effect based on the Lieb-Mattis theorem and will stimulate studies on topological properties in mixed spin chains.

Methods

We synthesized 4-Br-*o*-MePy-V using a conventional procedure²⁵ and prepared an iodide salt of the radical cation (4-Br-*o*-MePy-V)I using a reported procedure for salts with similar chemical structures²⁶. 1-butyl-3-methylimidazolium tetrachloroferrate (239 mg, 0.71 mmol) was slowly added to a solution of (4-Br-*o*-MePy-V)I (149 mg, 0.28 mmol) in 10 ml of ethanol and stirred for 40 min. The dark-green solid (4-Br-*o*-MePy-V)FeCl₄ was then separated by filtration. The dark-green residue was recrystallized using mixed solvent of acetonitrile and methanol. The crystal structure was determined on the basis of intensity data collected using a Rigaku AFC-8R Mercury CCD RA-Micro7 diffractometer. High-field magnetization measurement in pulsed magnetic fields of up to approximately 53 T was conducted using a nondestructive pulse magnet. The magnetic susceptibility was measured using a commercial SQUID magnetometer (MPMS-XL, Quantum Design). The experimental result was corrected for the diamagnetic contributions calculated by Pascal's method. The specific heat was measured using a commercial calorimeter (PPMS, Quantum Design) by using a thermal relaxation method. Considering the isotropic nature of organic radical systems, all experiments were performed using small randomly oriented single crystals. *Ab initio* MO calculations were performed using the UB3LYP method with the basis set 6-31 G(d,p) in the Gaussian 09 program package. For the estimation of intermolecular magnetic interaction, we applied our evaluation scheme that have been studied previously²⁷. The QMC code is based on the directed loop algorithm in the stochastic series expansion representation²⁸. The calculations for the mixed spin-(1/2, 5/2) Heisenberg chain were performed for $N = 128$ under the periodic boundary condition, where N denotes the system size. It was confirmed that there is no significant size-dependent effect. All calculations were carried out using the ALPS application^{29,30}.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

H.Y. planned the study. H.Y., T.O., Y.I., N.U. and Y.H. performed sample preparation and characterization. H.Y., Y.I., Y.K., T. Kawakami and M.H. discussed the results. H.Y., T.O., T. Kida, A.M. and M.H. performed the experiments. H.Y. wrote the manuscript with contributions from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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