Elementary Excitation in the Haldane State

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A localized two-spin bound state with the resultant spin $S=1$ is proposed as an elementary excitation of the Haldane state in $Ni(C_2H_8N_2)NO_2(ClO_4)$ (NENP) and $Ni(C_3H_{10}N_2)NO_2(ClO_4)$ (NINO). The bound state corresponds to the lowest excited triplet and behaves like a soliton or a small exciton. An ESR study has been done and the resonance of the two-spin bound state is observed. The result is satisfactorily explained by the spin-cluster model and supports the Haldane conjecture. Various magnetic properties of NENP and NINO are well explained by the present model.

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There has been increasing interest in the energy-gap problem of the linear-chain Heisenberg antiferromagnet with spin $S=1$ since Haldane[1] conjectured that the chain composed of integer spins has an energy gap above the ground state, which is called the Haldane state in this Letter. Much theoretical work[2-7] supports the conjecture. The corresponding experimental tests, however, are not conclusive at present, mainly because of the difficulty in getting typical materials suitable for the gap measurement. $CsNiCl_3$ is one of the candidates and a gap has been reported by neutron diffraction,[8,9] but the interchain interactions are not negligible and the ideal Haldane state is difficult to see below the Néel temperature of 4.9 K. Renard *et al.*[10,11] have done magnetic and neutron-diffraction experiments on NENP and NINO with the chemical formulas $Ni(C_2H_8N_2)NO_2(ClO_4)$ and $Ni(C_3H_{10}N_2)NO_2(ClO_4)$, respectively, which are regarded as better materials for testing the gap. The chains are parallel to the b axis, and the high-temperature magnetic susceptibilities shown in Fig. 1 are well understood by the antiferromagnetic linear-chain model with an intrachain exchange J of 47.5 K and positive uniaxial anisotropy DS_z^2 with an energy of 12 K. No long-range order is found down to 1.2 K, reflecting negligible interchain interactions, and exponentially decreasing susceptibility at low temperatures shows the presence of the energy gap.

Recently, a high-field magnetization study up to 50 T (Tesla) was done by Katsumata *et al.*,[12] and field-induced quenching of the gap is found, as is shown in Fig. 1. A linear magnetization appears above the critical field H_T which is angular dependent. Similar data were obtained by Ajiro *et al.*[13] H_T is attributed to the crossover field between the ground state and a sublevel of the excited triplet which lies at the bottom of the spin-wave continuum.[2,12] The main anisotropy of H_T comes from an effective DS_z^2 term defined in the triplet, and the gap energy and D have been estimated. Then, one of the next steps is to find the triplet directly by the spectroscopic method.

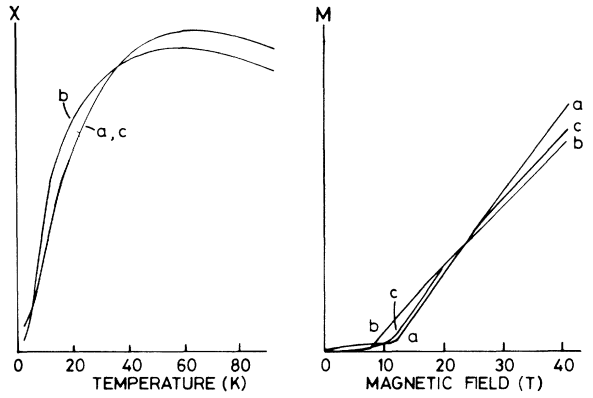

FIG. 1. Sketches of the magnetic susceptibility (Ref. 10) and high-field magnetization (Ref. 12) in NENP.

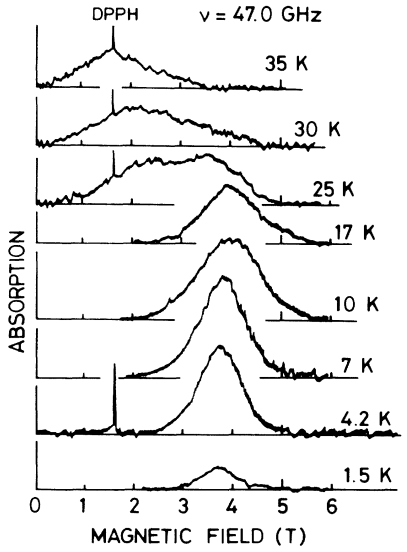

FIG. 2. Temperature dependence of the ESR signal in NENP on a relative scale. Magnetic field is applied in the a-c plane at an angle of 30° from the a axis.

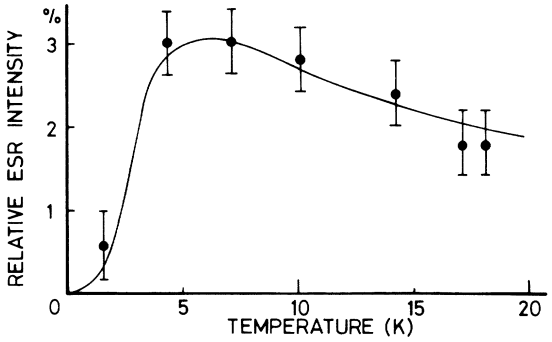

FIG. 3. Temperature dependence of the ESR intensity. % denotes the effective percentage of spins responsible for ESR.

An electron-spin-resonance (ESR) study has been done with millimeter waves in the 45-GHz region under a pulsed magnetic field up to 10 T. The technical details are given elsewhere.[14] A broad paramagnetic resonance is found from room temperature down to about 35 K with $g=2$, and it is understood by exchange-mixed paramagnetic resonance where the fine-structure components are amalgamated by the intrachain exchange interaction. The linewidth is temperature dependent and the shape is in between Gaussian and Lorentzian, reflecting the one-dimensional spin correlations.

A new resonance line with width of about 1 T is found below about 20 K where the paramagnetic resonance disappears, as is seen in Fig. 2. The absorption intensity decreases below 7 K, as is shown in Fig. 3, which means that the signal comes from excited states. The angular dependences of the resonance field in NENP and NINO are shown in Fig. 4. The observed results are not explained by the antiferromagnetic resonance (AFMR) model. The usual AFMR theory in NENP and NINO in the 45-GHz region predicts two peaks near 10 T only around the spin easy axis, which does not explain the experimental results. Moreover, the observed resonance intensity decreases below 4.2 K, which is also inconsistent with the AFMR theory.

The results are explained by assuming an effective Hamiltonian for the triplet given by

$$H=\mu_B SgH+D\{S_z^2-\tfrac{1}{3}S(S+1)\}+E(S_x^2-S_y^2)\,, \quad (1)$$

where the first term is the Zeeman energy with $S=1$ and the other terms give the orthorhombic anisotropy. The center of the triplet is above the Haldane ground state with energy E_G. The parameters obtained are $g=2.2$, $D=-11$ K (-7.5 cm^{-1}), and $E=-0.92$ K (-0.67 cm^{-1}) for NENP and $g=2.2$, $D=-16$ K (-12 cm^{-1}), and $E=1.5$ K (1.1 cm^{-1}) for NINO. It is noted that the resonance along the a axis is found at 5 T in NENP, while no corresponding resonance is found in NINO where the resonance shows a loop in the a-c plane. The latter pattern is expected when $E>0.78$ cm^{-1} at 47 GHz. The energy gap is obtained by using the critical-field formula along the b axis, given by

$$H_T^b=\{(E_G-D/3)^2-E^2\}^{1/2}/g_b\mu_B\,, \quad (2)$$

where $g_b=2.15$ (Ref. 10) and $H_T^b=7.0$ T for NENP. Equation (2) is the extended formula of Eq. (2) in Ref. 12 where the E term is neglected. E_G is thus determined as 13 K (9.5 cm^{-1}) for both NENP and NINO. The values of g, D, E, and E_G obtained for them satisfactorily explain their magnetic properties, and the details will be published elsewhere.[15]

The energy-level diagram of NENP is shown in Fig. 5. The Haldane ground state is shown by the zero-energy line, and the excited triplet at E_G splits by the D and E

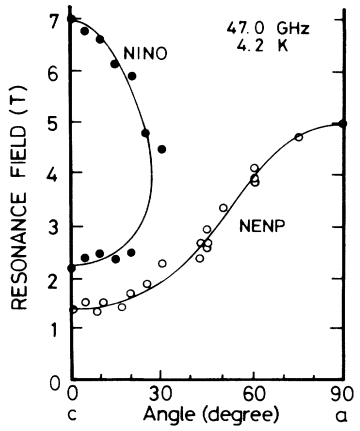

FIG. 4. Angular dependences of the resonance field. Solid curves are theoretically drawn by using values of g, D, and E in the text.

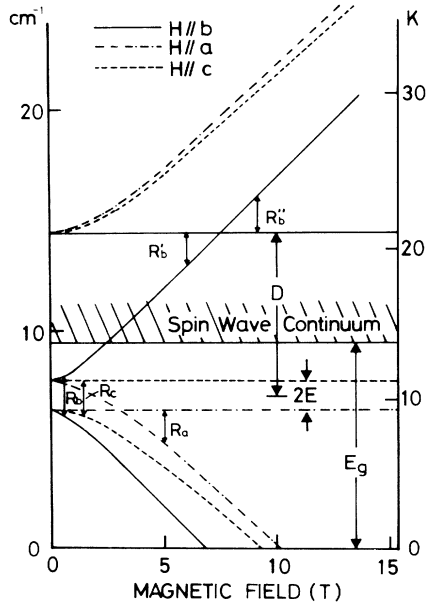

FIG. 5. Energy-level diagram under a magnetic field. The field dependence of spin-wave continuum is not shown.

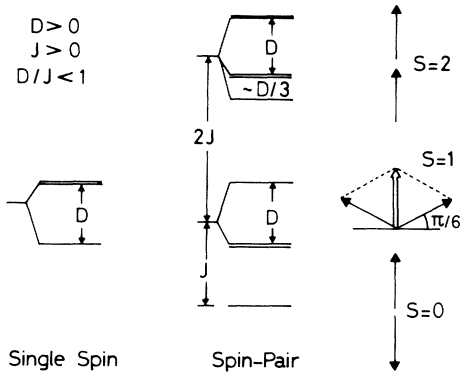

FIG. 6. Energy-level splittings of single-spin and spin-pair states.

terms into three singlets at zero magnetic field. These levels show the field dependences, and the crossover to the ground state occurs for each low-lying level at the corresponding critical field. The microwave transitions R_a, R_b, and R_c are experimentally observed but R_b' and R_b'' are not detected. The results are consistent with the gap model because levels in the spin-wave continuum are usually broadened so that no resonance is expected.

A remaining but important problem is the negative sign of D in the excited state. If the triplet were described by the usual spin wave on the chain, the D value should be positive, reflecting the anisotropy of the Ni^{2+} spin in this compound. Therefore, a new model is needed to explain the discrepancy. A hint of the problem is found in the exchange-coupled $S=1$ spin pair with positive D for each spin, expressed by the model Hamiltonian

$$H=\mu_B(S_1+S_2)gH+D(S_{1z}^2+S_{2z}^2)+JS_1S_2, \qquad (3)$$

where the first term represents the Zeeman energies of two spins S_1 and S_2. $D>0$ and $J>0$ with $D/J<1$ are assumed. The energy levels are obtained by solving a 9×9 determinant and the diagram for $H=0$ is shown in the center panel of Fig. 6. For comparison, single-spin levels with the same D value are shown on the left-hand side. The point is that the effective D value of the first excited triplet has the same magnitude as that of the single spin but the sign is opposite. The physical reason is qualitatively understood by looking at the vector model on the right-hand side of Fig. 6. When the resultant spin of the excited triplet (white arrow) points along the z axis, the main components of the S_1 and S_2 spins are perpendicular to the z axis so that the sign of D in the resultant spin should be negative.

With this in mind, the vector model of the excited triplet is sketched in Fig. 7. The triplet state may be regarded as a two-spin bound state with resultant spin $S=1$ running in a chain like a soliton or a small exciton with formation energy E_G. No long tails of the spin packet are expected because a large packet reduces the negative D value whose magnitude should be close to that in the

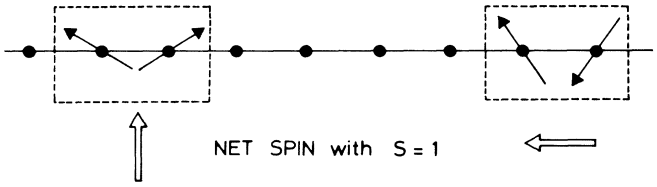

FIG. 7. Schematic models of the excited two-spin bound states with the resultant spin $S=1$.

two-spin model. Therefore, the excited triplet may be modeled by a localized spin cluster in a chain. The spin-cluster excitation was first found in the Ising-like ferromagnetic chain in $CoCl_2 2H_2O$.[16] The temperature dependence of the ESR absorption intensity calculated by the spin-cluster model is shown by the theoretical curve in Fig. 3, which shows satisfactory agreement with the experimental results. It is noted that the number of localized spin clusters in the Ising chain is obtained by a bosonlike excitation model[17] where the excitation energy gap corresponding to E_G is $2JS^2$, which is the formation energy of the spin cluster in a chain. In addition to E_G, D and E terms with the Zeeman energy are taken into account for the Haldane problem. The partition function of the three excited levels with the singlet Haldane ground state is calculated and the population numbers as a function of temperature are obtained. Excitation to the spin-wave continuum is neglected. The result is sketched by the Maxwell-Boltzmann distribution at low temperature, but a deviation appears at high temperatures because of the dense excitation. However, the following difference should be noticed: The mean-field model is applicable for calculation of the Ising-spin-cluster energy while it is not used for the Haldane triplet where the coupling is defined by E_G, which is difficult to estimate with the mean-field model.

The present model may explain the susceptibility crossover around 35 K shown in Fig. 1. The high-temperature susceptibility along the b axis is smaller than those for the a and c axes, reflecting the positive D value. At low temperatures, however, the main excitation is the two-spin bound state with negative D value, so that the susceptibility along the chain should be larger than the others.

The two-spin bound state in NENP and NINO suggests that the Haldane state may be understood in the framework of the theory of resonating valence bonds proposed by Anderson[18] and especially by the model of the valence-bond solid proposed by Affleck *et al.*[5] because the two-spin bound state is regarded as an excited valence-bond state of $S=1$ composed of two spins in a chain.

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[1]F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983); J. Appl. Phys. **57**, 3359 (1985).

[2]R. Botet, R. Jullien, and M. Kolb, Phys. Rev. B **28**, 3914 (1983).

[3]J. B. Parkinson and J. C. Bonner, Phys. Rev. B **32**, 4703 (1985); J. Appl. Phys. **61**, 3941 (1987).

[4]M. P. Nightingale and H. W. J. Blöte, Phys. Rev. B **33**, 659 (1986).

[5]I. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, Phys. Rev. Lett. **59**, 799 (1987).

[6]I. Affleck, Phys. Rev. Lett. **62**, 474 (1989).

[7]M. Takahashi, Phys. Rev. Lett. **62**, 2313 (1989).

[8]W. J. L. Buyers, R. M. Morra, R. L. Armstrong, M. J. Hogan, P. Gerlach, and K. Hirakawa, Phys. Rev. Lett. **56**, 371 (1986).

[9]M. Steiner, K. Kakurai, J. K. Kjems, D. Petitgrand, and R. Pynn, J. Appl. Phys. **61**, 3953 (1987).

[10]J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, and W. G. Stirling, Europhys. Lett. **3**, 945 (1987).

[11]J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod. J. Ribas, W. G. Stirling, and C. Vettier, J. Appl. Phys. **63**, 3538 (1988).

[12]K. Katsumata, H. Hori, T. Takeuchi, M. Date, A. Yamagishi, and J. P. Renard, Phys. Rev. Lett. **63**, 86 (1989).

[13]Y. Ajiro, T. Goto, H. Kikuchi, T. Sakakibara, and T. Inami, Phys. Rev. Lett. **63**, 1424 (1989).

[14]M. Date, IEEE Trans. Magn. **12**, 1024 (1976).

[15]T. Takeuchi, M. Ono, H. Hori, T. Yosida, and M. Date, J. Phys. Soc. Jpn. (to be published).

[16]M. Date and M. Motokawa, Phys. Rev. Lett. **16**, 1111 (1966).

[17]M. Date and M. Motokawa, J. Phys. Soc. Jpn. **24**, 41 (1968).

[18]P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).