

## Experimental Verification of the Gapless Point in the $S = 1$ Antiferromagnetic Bond Alternating Chain

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(Received 7 July 1997)

Susceptibility and high field magnetization measurements have been performed on powdered samples of  $[\{\text{Ni}(\text{333-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  [333-tet denotes tetraamine  $N, N'$ -bis(3-aminopropyl)-1,3-propanediamine]. As the temperature is decreased, the susceptibility exhibits a smooth maximum around 120 K and decreases gradually down to 10 K, and then decreases rapidly. Magnetization up to 50 T at 1.4 K shows no gap in this compound within the experimental accuracy. We have carried out numerical calculations for the  $S = 1$  antiferromagnetic bond alternating chain and obtained very good agreement between experiments and calculations for the alternating ratio  $\alpha = 0.6$ . [S0031-9007(97)05217-4]

PACS numbers: 75.10.Jm, 75.50.-y, 75.50.Ee

Experimental and theoretical efforts on low dimensional magnetic systems have brought about a profound understanding of physics in many body quantum systems. In particular, linear chain Heisenberg antiferromagnets (LCHA's) with the spin quantum number  $S = 1$  have been studied extensively [1–3] in connection with Haldane's conjecture [4] that there is an energy gap between the ground state and the first excited one for integer  $S$ , while not for half-odd integer  $S$ . Recently, low dimensional oxide systems, such as inorganic spin-Peierls systems [5,6] and spin ladder systems [7,8], have attracted a lot of interest.

One of the recent interesting topics in  $S = 1$  LCHA's is bond alternation. Using the Hamiltonian for the  $S = 1$  bond alternating chain given by  $\mathcal{H} = \sum_i \{1 - (-1)^i \delta\} \mathbf{S}_i \cdot \mathbf{S}_{i+1}$  where  $\delta$  ( $0 \leq \delta \leq 1$ ) is the parameter representing bond alternation and  $\mathbf{S}_i, \mathbf{S}_{i+1}$   $S = 1$  spin operators, Affleck and Haldane [9] predicted that there is a massless (gapless) point at a certain alternating ratio  $\delta_c$ . Subsequent numerical studies [10–15] estimated the critical ratio  $\delta_c$  as 0.25. Moreover, it was shown numerically that the ground state is in the Haldane or the singlet dimer phase depending on  $\delta$  ( $0.0 \leq \delta < 0.25$  for the former and  $0.25 < \delta \leq 1.0$  for the latter).

In recent years, some Ni bond alternating compounds [16–19] were synthesized and the magnetic properties were studied. They were (a) *catena*- $[\{\text{Ni}_2(\mu\text{-N}_3)_3(\text{dpt})_2\}_n](\text{ClO}_4)_n$  [dpt denotes bis(3-aminopropyl)amine], (b)  $\{\text{Ni}_2(\text{EDTA})(\text{H}_2\text{O})_4\}_n \cdot (2\text{H}_2\text{O})_n$  (EDTA denotes ethylenediaminetetraacetic acid), (c) *trans*- $[\{\text{Ni}(\text{333-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  [333-tet denotes  $N, N'$ -bis(3-aminopropyl)-1,3-propanediamine], (d)  $[\{\text{Ni}_2(\text{dpt})_2(\mu\text{-ox})(\mu\text{-N}_3)\}_n](\text{PF}_6)_n$  (ox denotes  $\text{C}_2\text{O}_4$ ), and (e)  $[\{\text{Ni}_2(\text{Medpt})_2(\mu\text{-ox})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  [Medpt denotes methyl-bis(3-aminopropyl)amine]. Alternating

ratios  $\alpha$  of the neighboring exchange constants were obtained from the fit of the susceptibility to a formula calculated by Borrás-Almenar [20] using the Hamiltonian defined as

$$\mathcal{H} = J \sum_{i=1}^{N/2} (\mathbf{S}_{2i-1} \cdot \mathbf{S}_{2i} + \alpha \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1}). \quad (1)$$

However, no comparison between experiment and theory has been carried out from the viewpoint of verification of the phase separation and the gapless point. Note that the critical ratio  $\alpha_c$  corresponding to  $\delta_c$  is 0.6. Magnetization curves at zero Kelvin of the  $S = 1$  LCHA with bond alternation were calculated with the Hamiltonian  $\mathcal{H} = \sum_i \{1 - (-1)^i \delta\} \mathbf{S}_i \cdot \mathbf{S}_{i+1} - g \mu_B S_i^z H + D(S_i^z)^2$  where  $-g \mu_B S_i^z H$  is the Zeeman term,  $g$  the  $g$  value of  $\text{Ni}^{2+}$ ,  $\mu_B$  the Bohr magneton and  $H$  the external magnetic field, and  $D \sum_i (S_i^z)^2$  is the single ion anisotropy term [21]. One of the important features in this study is that a 1/2-plateau appears in the magnetization curve at least when  $0 < \delta \leq 1$  and  $D \geq 0.0$ . Quite recently, the above finding was generalized and it was argued that the magnetization per site  $m$  is topologically quantized as  $n(S - m) = \text{integer}$  at the plateaus, where  $n$  is the period of the ground state [22]. Accordingly, in the  $S = 1$  antiferromagnetic bond alternating chain ( $n = 2$ ),  $m = 1/2$  can be quantized in addition to  $m = 0$  and 1. Under such circumstances, some of the authors performed magnetization measurements on some of these compounds and observed 1/2-plateaus in magnetization curves of  $\{\text{Ni}_2(\text{EDTA})(\text{H}_2\text{O})_4\}_n \cdot (2\text{H}_2\text{O})_n$  and  $[\{\text{Ni}_2(\text{Medpt})_2(\mu\text{-ox})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  [23].

In the present paper, we report the results of susceptibility and high field magnetization measurements performed on powdered samples of  $[\{\text{Ni}(\text{333-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$ . We have found that the experimental results show no or

a very small gap in this compound and verified that  $\alpha_c$  should be about 0.6 in comparison with some numerical results.

First, we mention the synthesis and the crystal structure of  $[\{\text{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$ . The compound  $[\{\text{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  was synthesized with a slow evaporation method from an aqueous solution containing equimolars of  $\text{Ni}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ , 333-tet ligand, and  $\text{NaN}_3$  according to Ref. [18]. This compound crystallizes in the triclinic system, space group  $P\bar{1}$ . The lattice constants and angles at room temperature are  $a = 8.765(1) \text{ \AA}$ ,  $b = 8.976(1) \text{ \AA}$ ,  $c = 11.995(2) \text{ \AA}$ ,  $\alpha = 106.65(1)^\circ$ ,  $\beta = 110.06(1)^\circ$  and  $\gamma = 91.11(1)^\circ$ . Each Ni atom is placed in an octahedral environment and links to the neighboring Ni atoms via azido ( $\text{N}_3$ ) groups to form the chain structure along the  $c$  axis. The chain structure of this compound is shown in Fig. 1. Here, most of the ligand atoms and the counter anions  $\text{ClO}_4^-$  are omitted for simplicity. The neighboring chains are well separated from each other by  $\text{ClO}_4^-$  anions. Two kinds of alternating centrosymmetric azido bridges are present in the chain. The Ni-N bond distances and Ni-N-N bond angles for these azido bridges are  $2.077(3) \text{ \AA}$ ,  $142.4(3)^\circ$  and  $2.204(3) \text{ \AA}$ ,  $123.6(2)^\circ$ , respectively, giving bond alternation in the chain. Susceptibility ( $M/H$ ) was measured at 100 Oe with SQUID magnetometer (Quantum Design's MPMS2) in RIKEN and high field magnetization measurements were done by using a pulse magnet

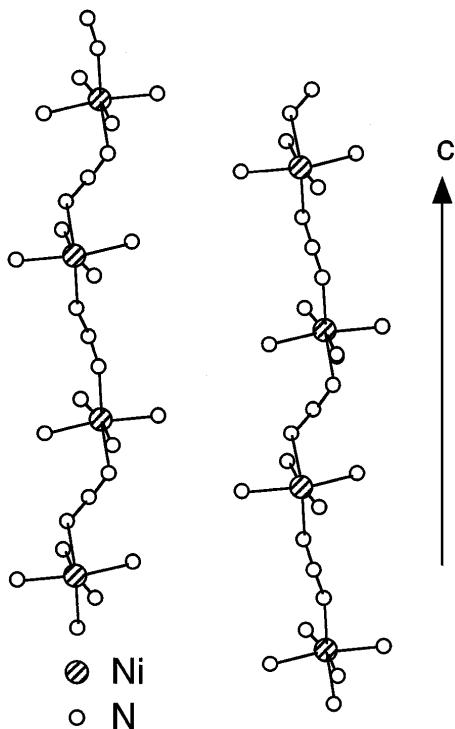


FIG. 1. Schematic view of the chain structure of  $[\{\text{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$ . Most parts of the 333-tet ligands and  $\text{ClO}_4^-$  anions are omitted for simplicity.

with the duration time of about  $400 \mu\text{sec}$  up to 50 T at KYOKUGEN in Osaka University. In the magnetization measurements, we used the powdered sample of 39.7 mg (formula weight 388.50) filled inside a cylindrical tube with 2.4 mm diameter and 9.5 mm length. The experiments were performed with the induction method [24], so that the field derivative of magnetization  $dM/dH$  should be detected very sensitively and the relative sensitivity is estimated to be about  $10^{-8} \text{ emu}$ .

Susceptibility of the powdered sample of  $[\{\text{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  is shown in Fig. 2. A round maximum appears around 120 K and the susceptibility decreases gradually down to 10 K, and then it decreases steeply as the temperature is decreased further. No long range order was observed down to 1.8 K. The behavior of the susceptibility at low temperatures below about 30 K is quite similar to that of the  $S = 1/2$  LCHA which was calculated recently by the Bethe ansatz and field theory methods [25] and observed experimentally in an organic ion radical salt [3,3'-dimethyl-2,2'-thiazolinocyanine]-TCNQ [26]. From the similarity of these findings, we can say that this system is gapless or nearly gapless because of a convex fall down, which is similar to a logarithmic curve, in the susceptibility at low temperatures [27]. We compare the susceptibility with some numerical calculations [an exact diagonalization method and a quantum Monte Carlo (QMC) method (loop algorithm) [28]] for the Hamiltonian (1), including the single ion anisotropy term for the former case. In the former calculation, the susceptibilities at and around the gapless points predicted in the  $D$  versus  $\alpha$  plane [21] are calculated and compared with the experimental one. Then, we conclude that the susceptibility can be fitted for a small  $D/J$  ( $< 0.1$ ),  $\alpha$  around 0.6 and  $J/k_B \sim 100 \text{ K}$ .

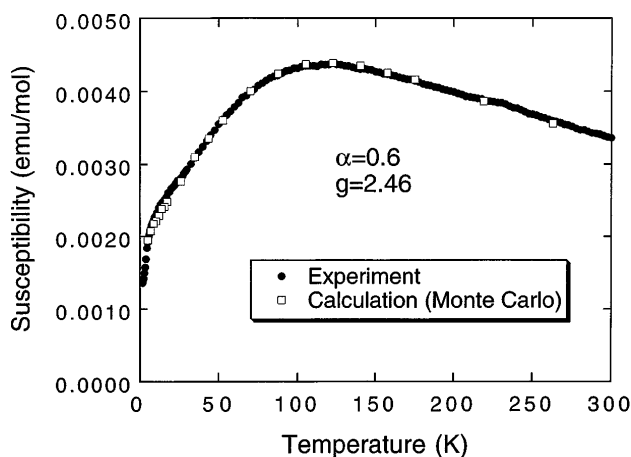


FIG. 2. Temperature dependence of the susceptibility ( $M/H$ ) of a powdered sample of  $[\{\text{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  (filled circles). Open squares show the calculated data by means of a quantum Monte Carlo (QMC) method for 96 sites for the  $S = 1$  bond alternating chain with the bond alternating ratio  $\alpha = 0.6$ .

This small  $D/J$  is reasonable, because  $\text{Ni}^{2+}$  ion under an octahedral ligand field usually has the  $D/k_B$  value varying from 1 to 10 K. For  $D/k_B T \ll 1$ , the susceptibility for a powdered sample can be compared with the calculated one for  $D = 0$ . In Fig. 2, open squares show the results of the QMC method for 96 sites with  $\alpha = 0.6$ . The exchange constant  $J/k_B$  is estimated to be 110 K with the  $g$  value of 2.46. The agreement between experiment and calculation is very good. We show  $\alpha$  dependence of the susceptibilities calculated by means of the QMC method (96 sites) in Fig. 3. Here, we take the exchange constants and the  $g$  values to fit the experimental data around 300 K. The susceptibilities except for  $\alpha = 0.6$  decrease exponentially at low temperatures. It is easily mentioned from the calculated susceptibilities that the critical alternating ratio which corresponds to the gapless point should exist at about 0.6. Details and further results of the Monte Carlo calculation is presented in a longer paper [29].

In order to confirm that this is a gapless or a nearly gapless system, we carried out high field magnetization measurements. The result is shown in Fig. 4 together with the result of a numerical calculation for  $\alpha = 0.6$  at zero Kelvin made by the product-wave-function renormalization-group (PWFRG) method [30]. The PWFRG method has been verified [31] to be more useful for investigation of the magnetization process than the original density-matrix renormalization-group method devised by White [32]. The agreement between experiment and theory is also very good and the estimated exchange constant  $J/k_B$  is 115 K, which is close to that obtained from the susceptibility fitting (110 K). The slope of the magnetization  $dM/dH$  at zero field is about 10 times larger than the sensitivity of this measuring system. Therefore, we can conclude that this compound has no gap within the experimental accuracy and the gapless point should exist at about  $\alpha = 0.6$ . In the inset

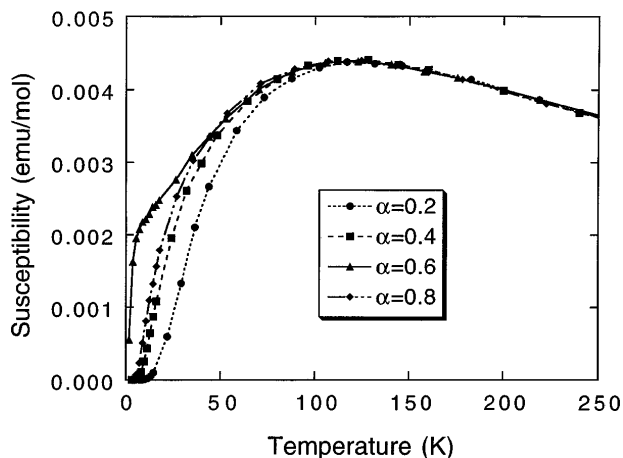


FIG. 3. Bond alternating ratio  $\alpha$  dependence of the susceptibility calculated with a QMC method (96 sites).

of Fig. 4, full magnetization curves up to the saturation field calculated by the PWFRG and a method introduced by Sakai and Takahashi (ST) [33] are shown, together with experimental data. According to the calculation, a  $1/2$ -plateau of magnetization curve, which is characteristic of the  $S = 1$  bond alternating chains, should be expected around 140 T.

In conclusion, we have performed susceptibility and magnetization measurements on an  $S = 1$  antiferromagnetic bond alternating chain compound  $[\{\text{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$ . The susceptibility exhibits the behavior of a convex curve below about 10 K similar to a logarithmic fall down which is typical of the gapless antiferromagnetic chain. By comparing experimental results with some numerical calculations for the  $S = 1$  bond alternating chain with  $\alpha = 0.6$ , we have obtained a very good agreement and evaluated the exchange constant  $J/k_B = 110 \sim 115$  K and the  $g$  value of  $\text{Ni}^{2+}$  ion  $g = 2.46$ . Consequently, we have verified experimentally that the gapless point should exist at about  $\alpha = 0.6$ .

This work was carried out under the Visiting Researcher's program of KYOKUGEN in Osaka University. The authors thank the Supercomputer Center of Institute for Solid State Physics, University of Tokyo, for the facilities and the use of the FACOM VPP500. Part of the calculations were performed on the Intel Japan PARAGON at the Institute for Solid State Physics, University of Tokyo. Some of the computer programs are based on KOBEPACK VER.1.0 coded by Professor T. Tonegawa, Professor M. Kaburagi, and Dr. T. Nishino. The computer program for PWFRG calculations is based on the

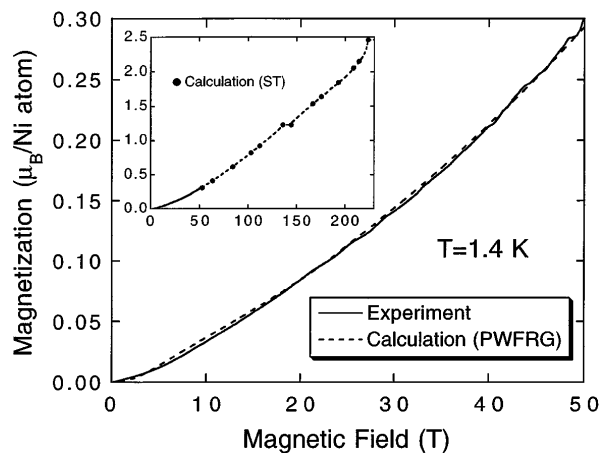


FIG. 4. Magnetization of a powdered sample of  $[\{\text{Ni}(333\text{-tet})(\mu\text{-N}_3)\}_n](\text{ClO}_4)_n$  at 1.4 K versus magnetic field up to 50 T. The broken line shows a magnetization curve at 0 K calculated with the product-wave-function renormalization-group (PWFRG) method. Inset: Calculated magnetization curves up to the saturation field by the PWFRG method (broken line) and a method introduced by Sakai and Takahashi (ST) (filled circles), together with experimental data (solid line).

one coded by Mr. K. Okunishi. R.S. thanks him for it and useful discussions. R.S. also thanks the Yukawa Institute for Theoretical Physics for the use of the NEC SX4 and the Akutsu group, Osaka University for the use of the workstation HP 9000 C180XP. This study was partially supported by a Grand-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, Sports and Culture.

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