Magnetization Process of an $S=1$ Linear-Chain Heisenberg Antiferromagnet

K. Katsumata
The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

H. Hori, T. Takeuchi, and M. Date
Department of Physics, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

A. Yamagishi
The Research Center for Extreme Materials, Osaka University, Toyonaka, Osaka 560, Japan

J. P. Renard
Institut d'Electronique Fondamentale, Bâtiment 220, Université Paris-Sud, 91405 Orsay CEDEX, France
(Received 10 April 1989)

Magnetization measurements in strong pulsed magnetic fields on single-crystal samples of the $S=1$ linear-chain Heisenberg antiferromagnet $Ni(C_2H_8N_2)_2NO_2(ClO_4)$ are reported. The magnetization is very small in the low-field region and begins to increase sharply at a finite field for all three of the principal axes. This is evidence for the existence of the Haldane gap in this compound.

PACS numbers: 75.60.Ej, 75.10.Jm, 75.50.Ee

Several years ago, Haldane[1] conjectured that the excitation spectrum of linear-chain Heisenberg antiferromagnets (LCHA) with integer spin values might be quite different from that for half-integer spin values; the former has a gap, while the latter does not. A number of theoretical works[2-9] have been published concerning this conjecture. Most of the results seem to be consistent with the Haldane's conjecture. Moreover, it has been argued that the Haldane gap problem is profoundly related to the quantum Hall effect[6] on one hand, and to elementary particle physics[7,8] on the other. So, Haldane's conjecture may be interesting to many physicists working in different fields.

The number of experiments which have tried to observe the Haldane gap is few. Buyers *et al.*[10] and Steiner *et al.*[11] have observed an energy gap in the $S=1$ LCHA system $CsNiCl_3$ in the short-range-ordered phase above the Néel temperature (T_N). By use of the parameters of the spin Hamiltonian obtained from the neutron scattering study below T_N, these authors could conclude that the energy gap observed above T_N cannot be explained by the effect of the single-ion anisotropy. Then, they suggest that their experiments support the existence of the Haldane gap which originates from the exchange interaction. Renard *et al.*[12,13] have done magnetic and neutron scattering measurements on the $S=1$ LCHA compound $Ni(C_2H_8N_2)_2NO_2(ClO_4)$, abbreviated NENP. This compound is a better candidate for an $S=1$ LCHA than $CsNiCl_3$ because (i) no three-dimensional long-range magnetic order exists down to 1.2 K ($T_N \cong 4.9$ K for $CsNiCl_3$), and (ii) the intrachain exchange interaction of NENP is about 3 times larger than that of $CsNiCl_3$. Renard *et al.* showed that their experimental results are consistent with Haldane's conjecture. In these circumstances, experiments on $S=1$ LCHA systems are clearly needed. In particular, the behavior of these systems in external magnetic fields is of great importance, since the Haldane gap energy is expected to be sensitive to magnetic fields[4] and we have a chance to control it with the fields. In this paper, we report the results of magnetization measurements on single-crystal samples of NENP in strong pulsed magnetic fields, and compare the results with the theory.

First we summarize the crystal and magnetic properties of NENP. This compound crystallizes in the orthorhombic system.[14] The lattice constants are $a=15.223$ Å, $b=10.300$ Å, and $c=8.295$ Å. The structure consists of $Ni(C_2H_8N_2)_2NO_2$ chains along the b axis. These chains are well separated from each other by ClO_4 molecules. The magnetic susceptibility measurements[13,14] on a single-crystal sample of NENP revealed a rounded maximum around 60 K along the three principal axes. The susceptibility data are well fitted with the results of the theoretical calculation for the $S=1$ LCHA using the following values:[14] $J=-47.5$ K, $g_a=2.23$, $g_b=2.15$, and $g_c=2.21$, where J is the intrachain exchange constant and the g's are the g values along the crystalline axes. The value of the single-ion anisotropy constant (D) is also estimated from the susceptibility data[14] to be $D=0.9$ K. Renard *et al.*[13] have obtained a value for D about 10 times larger. In both cases the quantization axis for the single-ion anisotropy term (DS_z^2) is taken to be parallel to the crystalline b axis.

We show in Fig. 1 the magnetization (M) curves along the three principal axes of NENP versus the external magnetic field (H). A noteworthy feature of the $M(H)$ curves is the sharp increase in M around 12 and 8 T for the perpendicular and parallel directions with respect to the chain axis. No hysteresis has been observed in the $M(H)$ curves within the experimental accu-

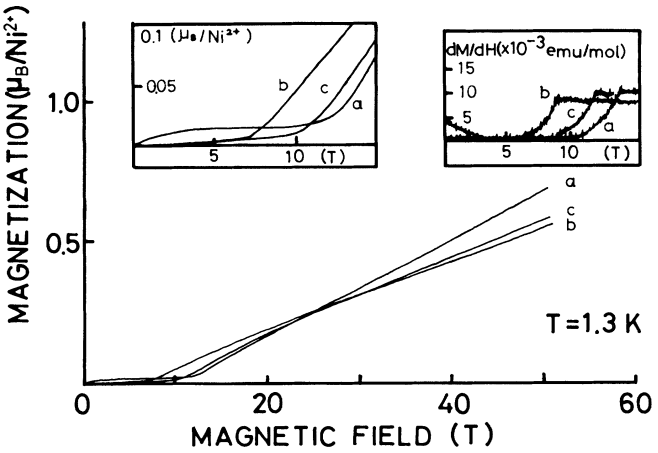

FIG. 1. The magnetization curves along the crystalline a, b, and c axes of NENP obtained at $T=1.3$ K. Inset (left): Low-field part of the magnetization curves. Inset (right): Corresponding dM/dH vs H curves obtained in the pulsed-field experiment. If we take the midpoints of the steplike dM/dH curves, the values of the transition fields along the a, b, and c axes are 13, 7.5, and 11 T, respectively.

racy (~0.2 T). Possible explanations for the existence of the state with low net moment in the low-field region of the NENP would be that it is due to (i) the Haldane gap, or (ii) a singlet ground state caused by the single-ion anisotropy term. The dimerized state formed by the spin-Peierls mechanism is unlikely to exist, since the Ni^{2+} ion has no orbital angular momentum in the ground state and thus the interaction between the spin and lattice is small. We discuss the possibility of the singlet ground state caused by the single-ion anisotropy. As was described before, NENP has a single-ion anisotropy term (DS_z^2, $Z\|b$). If D is positive and large, a ground state with $S_z=0$ would result, which is nonmagnetic. When H is applied along the b axis, the energy of the excited state with $S_z=-1$ decreases with the field strength and at a critical value (H_C) of H, becomes equal to that for $S_z=0$. In the field region above H_C, the system has a magnetic moment. When H is applied perpendicular to b, the sharp transition from the nonmagnetic to magnetic state does not happen. Instead, the magnetization gradually develops because in this case, the energy levels do not cross at finite fields. Our experiment on the single crystals shows clearly that a sharp change in M takes place for all of the principal axes. From this result, we can rule out the possibility of the singlet ground state due to the DS_z^2 term. Then, it is natural to conclude that the state with low net moment observed in the low-field region of NENP is formed by Haldane's mechanism. When an energy gap exists between the ground and excited states in an LCHA system, at low temperatures the spins tend to couple antiferromagnetically to form a singlet, and thus becomes nonmagnetic. When we apply large H to break the energy gap, the system becomes magnetic. This explains qualitatively what we have observed (Fig. 1).

There is an anisotropy in the transition field (H_T) from the nonmagnetic to magnetic state. This is consistent with the anisotropic temperature behavior of the magnetic susceptibility. Indeed, by fitting the low-temperature susceptibility data, two different gap values $E_G^{\|}=11$ K and $E_G^{\perp}=17$ K have been obtained for respective field directions parallel and perpendicular to the chain axis.[13] We discuss the possible origin of the anisotropy in the transition field. First, it is noted that the difference in the g value along the crystalline axes is too small to explain the anisotropy. The nature of the excited states in the $S=1$ LCHA system is not clear at present. However, it is reasonable to say that the first excited state is composed of a triplet because the excitation from the singlet ground state produced a magnetic moment at a site in the chain which takes three states ($S_z=1,0,-1$). This single-site excitation can move along the chain due to the exchange interaction. Botet, Jullien, and Kolb[3] have made finite-size-scaling studies on the $S=1$ LCHA with the single-ion anisotropy term. They showed that the Haldane gap energy decreases with increasing value of D irrespective of its sign. The lowest excited state they considered is a doublet for $D>0$. This means that the effect of D on the excitation in the $S=1$ LCHA system is reversed from that on the ground state. We take a negative sign for D in the excited state to discuss the anisotropic behavior of H_T.

For H applied along the b axis of NENP, the energy (E) of one of the excited doublet decreases as

$$E=E_G-|D|/3-g_{\|}\mu_B H\,, \tag{1}$$

where $E_G-|D|/3$ is the Haldane gap energy in zero external field and $g_{\|}$ the g value along the b axis. Then, the gap energy becomes zero at the transition field given by

$$H_T^{\|}=(E_G-|D|/3)/g_{\|}\mu_B\,. \tag{2}$$

When H is directed perpendicular to the b axis of NENP, the field-dependent gap energy is expressed as

$$E=E_G+|D|/6-(D^2+4g_{\perp}^2\mu_B^2H^2)^{1/2}/2\,. \tag{3}$$

The transition field perpendicular to the b axis is given by

$$H_T^{\perp}=(E_G^2+E_G|D|/3-2D^2/9)^{1/2}/g_{\perp}\mu_B\,. \tag{4}$$

Putting the experimental values for H_T^{α} and g_{α} ($\alpha=\|,\perp$) into Eqs. (2) and (4), we obtain the values 17 K for E_G and 16 K for D. The value of E_G is the same as that of $E_G^{\perp}$ estimated from the susceptibility data,[13] while the D value is slightly larger than that estimated before ($D\cong 12$ K).[13]

In Fig. 2 we compare the experiment with the theory.[4]

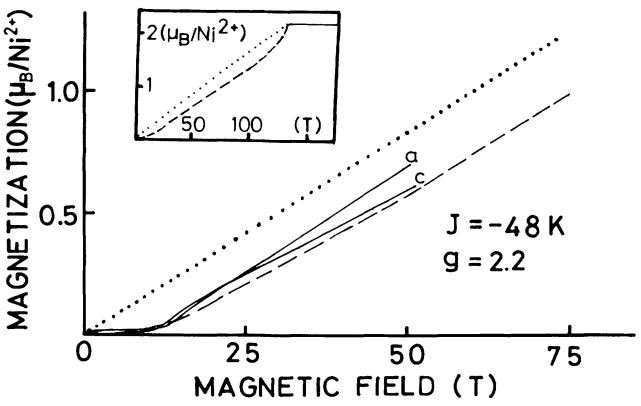

FIG. 2. The magnetization curves of NENP obtained from the present experiment compared with the result of the numerical calculation (dashed line) by Parkinson and Bonner on an $S=1$ linear-chain Heisenberg antiferromagnet. The dotted line is the result of the molecular-field calculation. Inset: Theoretical magnetization curves up to saturation.

Parkinson and Bonner[4] have done numerical studies on finite-size Heisenberg antiferromagnetic chain. They have obtained the $M(H)$ curve for an $S=1$ LCHA at $T=0$ K, which is shown in Fig. 2 by the dashed line. Here, we have used the values $g=2.2$ and $J=-48$ K determined from the susceptibility measurement.[14] Since the calculation is not accurate in the low-field region,[4] we compare the experiment with the theory in the high-field region above H_T. We have used the experimental $M(H)$ curve along the a and c axes in comparing it with the theory, because the theory does not consider the effect of D, and the spins tend to align into the a-c plane due to the single-ion ansiotropy term with positive D. The agreement between the theory and the experiment is satisfactory in the high-field region above H_T. From this result we confirm that NENP is a typical example of an $S=1$ linear-chain Heisenberg antiferromagnet.

Finally, we briefly discuss the fact that a finite magnetization remains along the a axis but not for the b and c axes (the upper left panel of Fig. 1). The $M(H)$ curve is reminiscent of the Brillouin curve seen in a paramagnet. This means that the finite magnetization comes from paramagnetic impurities. These impurities are not completely free but are coupled to host spins and point parallel to the a axis, because we do not see such a paramagnetic behavior of $M(H)$ along the b and c axes. A study of the effects of magnetic impurities on the Haldane gap is under way.

In conclusion, we have made magnetization measurements on single-crystal samples of NENP in magnetic fields up to 50 T. We have observed that the magnetization is very small in the low-field region and begins to increase sharply at a finite field for all three of the principal axes. We conclude that the existence of the state with low net moment in the low-field region followed by the sharp increase in M at H_T is evidence for the existence of the Haldane gap in NENP. We have successfully explained the anisotropy in H_T by taking a negative sign for D (D is positive in the ground state of NENP) in the excited triplet. A physical interpretation of this is postponed to a future study. The experimental $M(H)$ curve above H_T is in good agreement with the theory for an $S=1$ LCHA.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture. Institut d'Electronique Fondamentale is unité associé No. 22 du Centre National de la Recherche Scientifique.

[1]F. D. M. Haldane, Phys. Rev. Lett. **50**, 1153 (1983).
[2]R. Botet and R. Jullien, Phys. Rev. B **27**, 613 (1983).
[3]R. Botet, R. Jullien, and M. Kolb, Phys. Rev. B **28**, 3914 (1983).
[4]J. B. Parkinson and J. C. Bonner, Phys. Rev. B **32**, 4703 (1985).
[5]M. P. Nightingale and H. W. J. Blöte, Phys. Rev. B **33**, 659 (1986).
[6]I. Affleck, Nucl. Phys. **B265**, 409 (1986).
[7]I. Affleck, Phys. Rev. Lett. **56**, 408 (1986).
[8]I. Affleck, Phys. Rev. Lett. **57**, 1048 (1986).
[9]I. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, Phys. Rev. Lett. **59**, 799 (1987).
[10]W. J. L. Buyers, R. M. Morra, R. L. Armstrong, M. J. Hogan, P. Gerlach, and K. Hirakawa, Phys. Rev. Lett. **56**, 371 (1986).
[11]M. Steiner, K. Kakurai, J. K. Kjems, D. Petitgrand, and R. Pynn, J. Appl. Phys. **61**, 3953 (1987).
[12]J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, and W. G. Stirling, Europhys. Lett. **3**, 945 (1987).
[13]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).
[14]A. Meyer, A. Gleizes, J. Girerd, M. Verdaguer, and O. Kahn, Inorg. Chem. **21**, 1729 (1982).