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Haldane Gap System: Electronic Structures and Magnetic Properties

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The electronic structure of typical $s = 1$ Haldane gap compounds such as $[Ni(NH_2(CH_2)_3NH_2)_2N_3]ClO_4$ (NINAZ), $[Ni(NH_2CH_2C(CH_3)_2CH_2NH_2)_2N_3]ClO_4$ (NDMAZ) and $[Ni(NH_2CH_2C(CH_3)_2CH_2NH_2)_2N_3]PF_6$(NDMAP) have been investigated by means of discrete variational (DV)-Xα molecular orbital calculation. The DV-Xα calculations of these compounds reveal the importance of the overlap population analysis of bridging N_3^- ligands, suggesting the tendency of the well-balance intramolecular overlap dispersion in the bridged N_3^- molecule is correlated with the larger Haldane gap E_g.

Keywords: Haldane gap; electronic structure; DV-Xα molecular orbital calculation

INTRODUCTION

It is well known that there are many physical topics in the field of the low dimensional materials. Especially in the case of the magnetism,

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it is reported that the temperature dependence of the magnetic susceptibility of the one-dimensional (1D) Heisenberg antiferromagnet (HAF) is explained by the Bonner-Fisher theory[1]. On the other hand, Haldane predicted[2] that for the integer values of the spin s (s = 1, 2, 3...) the 1D Heisenberg antiferromagnet (1D-HAF) exhibits a singlet ground states separated from the first triplet excited state by a finite energy gap (Haldane gap E_g), while for half-odd integer s (s = 1/2, 3/2, 5/2...) the 1D-HAF has a gap-less spectrum of the excitations.

Among the quantum physics, there is no difference between integer and half-odd integer spins, because a 1/2 spin is used as an elementary unit in the quantum magnetism. However, Haldane's prediction is now well supported by many theoretical works and physical measurements[3]. After several years from Haldane's prediction, for the example, NENP[4], NINO, NINAZ, TMNIN were discovered as a typical materials in which the Haldane gap are observed by the magnetic measurements. Some materials have also been reported having a Haldane Gap and the chemical formula can be written as $[Ni(AA)_2X]Y$, ($(AA)_2$ = $(diamines)_2$, tetramines etc; $X = N_3^-$ and NO_2^-; $Y = ClO_4^-$, PF_6^- etc.)[5]. Quite particular theory called "Valence-Bond-Solid (VBS) state" should be available for explaining the mechanism of the Haldane gap only in the case of the integer spins.

In this paper, we will discuss the electronic structure and magnetic properties of $[Ni(NH_2(CH_2)_3NH_2)_2N_3]ClO_4$ (NINAZ), $[Ni(NH_2CH_2C(CH_3)_2CH_2NH_2)_2N_3]ClO_4$ (NDMAZ) and $[Ni(NH_2CH_2C(CH_3)_2CH_2NH_2)_2N_3]PF_6$ (NDMAP) in order to clarify the mechanism of the Haldane gap state and the correlation between the magnetic properties and the electronic structures of the Haldane gap system.

TABLE 1. Intra-chain exchange energy J and the Haldane Gap Eg of several Haldane gap system with the in-plane and bridging ligands and counteranions.

	counteranions					
	ClO_4^-			PF_6^-		
	in-plane ligands			in-plane ligands		
bridging ligands	dmpn	tn	en	dmpn	tn	en
N_3^-	J=-70.6K Eg=21.6K	J=-144K Eg=41K	gapless	J=-31K Eg=5K	J=-83.4K Eg=23K	J=-5.7K Eg=2.5K
NO_2^-	gapless	J=-49.9K Eg=14.2K	J=-47.5K Eg=17.0K	J=-9.0K Eg=3.5K	J=-3.0K Eg=1.5K	gapless

EXPERIMENTAL

We prepare several Haldane gap system compounds including Ni^{II} d^8 ion such as NINAZ, NDMAZ, NDMAP, NINOP[6], NINAP and NDMAPen by substituting several kinds of in-plane[7] and bridging ligands and counteranions. The magnetic susceptibility measurement of each sample is performed by a Quamtum Design MPMS-4 SQUID susceptometer operating at a magnetic field of 0.01 T between 2 and 300 K. A prismatic violet crystal (0.2 mm x 0.2 mm x 0.2 mm) was selected and mounted on a RIGAKU IP-Rapid diffractometer. Detailed structural data from X-ray diffractometer is applied to the constructing the cluster model for the DV-Xα calculation.

We summarize the correlation of the antiferromangetic interaction J and Haldane gap in the compounds with the counteranions, in-plane and bridging ligands in TABLE 1. As a consequence, we can reveal the possibility of controlling the Haldane gap by substituting the bridging (N_3^- > NO_2^-) and in-plane (tn > en > linear-tetramines > dmpn > Me_6[14]aneN_4 > [15]aneN_4) ligands and counteranions (ClO_4^-

TABLE 2. Crystallographic data for NINAZ, NDMAZ and NDMAP.

	NINAZ	NDMAZ	NDMAP
chem formula	$C_6H_{20}ClN_7NiO_4$	$C_{10}H_{28}ClN_7NiO_4$	$C_{10}H_{28}F_6N_7NiP$
fw	348.42	404.53	450.04
space group	Pnnm (#58)	C2 (#5)	Pnnm (#58)
T (K)	298	298	298
a (Å)	5.856	18.898	6.149
b (Å)	15.168	8.171	18.092
c (Å)	8.287	6.111	8.659
β (deg)	90	98.269	90
V (Å^3)	736.087	933.740	963.294
Z	2	2	2
λ (Å)	0.7107	0.7107	0.7107
ρ_{calcd} (g cm^{-1})	1.57	1.44	1.55
$R(F_0)$	8.6	5.8	8.9

> PF_6^-). From the X-ray structural analysis, the differences of the structure among these Haldane system materials are very small. So, the discussion only from the combination of the bridging and in-plane ligands and counteranion is not appropriate for the Haldane gap system, and an additional information of the electronic structure is required by means of DV-Xα molecular orbital calculation.

Cluster models for DV-Xα calculation

The crystallographic data of NINAZ, NDMAZ and NDMAP are collected in TABLE 2. These results are almost consistent with those reported previously[5]. The cluster model of each compound for DV-Xα calculation is cut off partially from the X-ray structural data of a single crystal. The cluster models of the same formula N-NiN_4-N_3-NiN_4-N are used by DV-Xα calculation in order to compare

both the electronic structure and the Haldane gap directly.

From the preliminary calculations using the smaller sizes of cluster models, we realize the importance of the larger size of in-plane ligand of cluster models without the influence of the terminal effects for DV-Xα calculations. In order to investigate the effect of the extended cluster size, the calculations which involve the complete structure of in-plane tn (tn = $NH_3(CH_2)_3NH_3$) ligands and the terminated NH_3 molecule were done, as shown in FIG. 1. As a result, we require the cluster model 1 (NH_3-Ni(tn)$_2$-NH_3-Ni(tn)$_2$-NH_3) on the basis of these preliminary calculation in order to clarify the subtle difference of the electronic structure among these three N_3-bridged compounds.

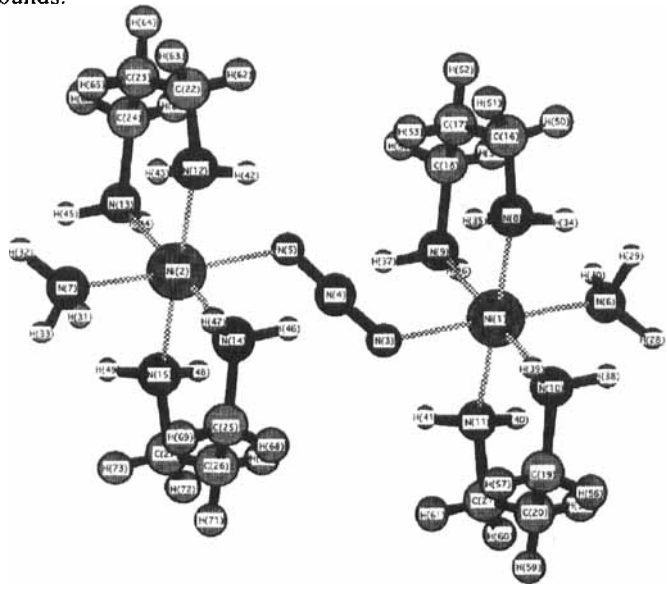

FIGURE 1. Cluster model NH_3-Ni(tn)$_2$-NH_3-Ni(tn)$_2$-NH_3 (model 1) of NINAZ for the DV-Xα calculations cut off partially from the X-ray structural data of a single crystal. The N_3 molecules of both ends are substituted to the NH_3 molecules in order to prevent the influence of the terminal molecular effect. The cluster models of NDMAZ and NDMAP are also employed by the same way.

Computational method

The non-relativistic DV-Xα calculation was performed with the Slater exchange parameter, α, of 0.7 for all atoms and with 5000 DV sampling points, which provided a precision of less than 0.1 eV for valence electron energy eigenvalues. We employed the basis functions of the nickel atom up to *4p* orbital, while those of the nitrogen and oxygen atoms were used up to *2p* orbitals. The calculations were carried out self-consistently until the difference in orbital populations between the initial and final states of the iteration was less than 0.01 electron/orbital. The computation details of the non-relativistic (DV-HFS) method used in the present work has been described elsewhere[8-10].

RESULTS AND DISCUSSION

In the N_3-bridged system, there is a stronger electron-electron interaction through the N_3^- molecule between two adjacent Ni spins than the NO_2-bridged compounds. The cluster model constructing on the basis of the accurate structure by X-ray diffractometer is used by the DV-Xα calculation for NINAZ, NDMAZ and NDMAP, which are typical Haldane system materials including N_3-bridging ligand.

The Haldane gaps are estimated by the magnetic measurement to be 41, 22 and 5 K for NINAZ, NDMAZ and NDMAP, respectively. From the analysis of the X-ray diffractometer, the distance between two adjacent Ni ions along the Haldane 1D chain is about 6 Å, suggesting that is too far to appear any antiferromagnetic interaction directly between them. Moreover, the structural differences among these three compounds are very small, suggesting that there is no possibility of taking place the strong super-exchange interaction

TABLE 3. Overlap population analysis of NINAZ, NDMAZ and NDMAP. The numbers in the parentheses with atom are corresponding to the numbers of the cluster model 1.

	NINAZ	NDMAZ	NDMAP
Ni(1)-N(3)	0.202	0.396	0.098
Ni(1)-N(6)	0.222	0.267	0.204
Ni(2)-N(5)	0.302	0.392	0.482
Ni(2)-N(7)	0.409	0.249	0.210
N(3)-N(4) a)	1.155	1.151	1.279
N(4)-N(5) b)	1.134	0.886	0.911
diff. (a-b)	0.021	0.265	0.368

between two Ni ions through N_3^- bridging ligands.

The calculated electronic level structure around the Fermi energy level of each cluster model is shown in FIG. 2. The features of their energy level structures are very similar to each other, reflecting almost

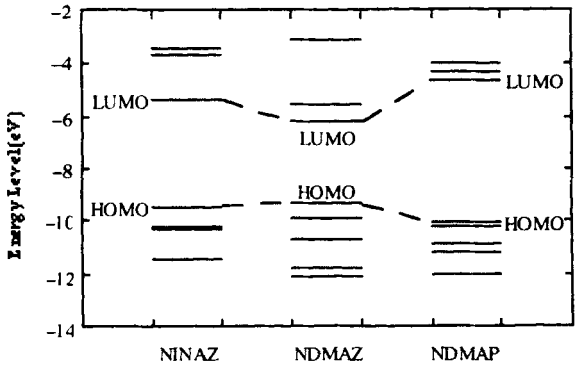

FIGURE 2. Electronic level structures of NINAZ, NDMAZ and NDMAP around the Fermi energy level (model 1).

the same X-ray structures. On the other hand, the amount of electrons of Ni *3d* orbitals is larger with the large Haldane gap material from the results of the Mulliken population analysis.

We have analyzed the overlap population between all neighboring atoms of each compound, as shown in TABLE 3, in order to clarify the correlation between the electronic structure and the Haldane gap more exactly. We suspect that the Haldane gap may be larger with large value of overlap population between -Ni-N_3-Ni- 1D chain, supporting the VBS state theory of Haldane gap system. From the result of the overlap population analysis, we reveal the tendency that the larger Haldane gap compound such as NINAZ has the well-balance intramolecular overlap dispersion in the bridged N_3^- molecule, whereas the smaller Haldane gap compound such as NDMAP has the large difference between two neighboring N-N overlap populations in the same bridging N_3^- molecule, as shown in TABLE 3. These results are explained as following; in the Haldane gap system, there is a strong spin-spin coupling between two neighboring opposite sign of $s = \pm 1$ spins along 1D chain through the way of the valence bond on the basis of VBS state. The strong antiferromagnetic interaction which is an origin of the Haldane gap is caused by its strong coupling between two spins. In the case of the N_3-bridged Haldane gap system compounds such as NINAZ, NDMAZ and NDMAP, N_3^- molecule between two adjacent Ni^{II} ions in 1D chain plays as a role of the coupler of VBS state between two neighboring opposite sign of $s = \pm 1$ spins. In the case of NINAZ, the difference of two N-N overlap population (N(3)-N(4) and N(4)-N(5)) in the N_3^- molecule is very small, suggesting that the well-balance dispersion of

the valence bond in the N_3^- molecule. As a result, the largest value of the Haldane gap is observed to be 41 K in the case of NINAZ. On the other hand, the overlap dispersion of NDMAP is inclined in the N_3^- molecule, suggesting that the small quantity of the Haldane gap is measured whose value is 5 K.

Only from the X-ray structural analysis, it is very difficult to find out these valence bond dispersions in 1D chain of the Haldane gap system compounds. So, an additional information of the electronic structure must be required in order discuss the correlation between the magnetic properties and the electronic structure through the overlap population analysis. As a result, we can reveal the new manifestation of the way to predict the value of the Haldane gap by means of the overlap population analysis by means of the DV-Xα molecular orbital calculation.

CONCLUSION

We reveal the possibility of controlling the Haldane gap value through the way of not only substituting the in-plane and bridging ligands and counteranions, but also the application of the predicted information from the DV-Xα molecular orbital calculation. The correlation of the observed Haldane gap *Eg* is in good agreement with the tendency of the dispersion of the intramolecular overlap population of each cluster model by means of the DV-Xα molecular orbital calculation.

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[4] (a) NENP = $[Ni(NH_2(CH_2)_2NH_2)_2NO_2]ClO_4$ (b) NINO = $[Ni(NH_2(CH_2)_3NH_2)_2NO_2]ClO_4$, (c) TMNIN = $(CH_3)_4N[Ni(NO_2)_3]$.
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[6] (a) NINOP = $[Ni(NH_2(CH_2)_3NH_2)_2NO_2]PF_6$, (b) NINAP = $[Ni(NH_2(CH_2)_3NH_2)_2N_3]$ PF_6, (c) NDMAPen = $[Ni(NH_2(CH_2)_2NH_2)_2N_3]PF_6$.
[7] tn = $NH_2(CH_2)_3NH_2$, en = $NH_2(CH_2)_2NH_2$, dmpn = $NH_2CH_2C(CH_3)_2CH_2NH_2$, Me_6[14]aneN4 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane.
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