Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Theoretical Study of the Antiferromagnetic Model Clusters for K_2MX_4 Type Solids

Taku Onishi [a], Tomohisa Soda [a], Yasutaka Kitagawa [a], Yu Takano [a], Daisuke Yamaki [a], Satoshi Takamizawa [a], Yasunori Yoshioka [a] & Kizashi Yamaguchi [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

Version of record first published: 24 Sep 2006

To cite this article: Taku Onishi, Tomohisa Soda, Yasutaka Kitagawa, Yu Takano, Daisuke Yamaki, Satoshi Takamizawa, Yasunori Yoshioka & Kizashi Yamaguchi (2000): Theoretical Study of the Antiferromagnetic Model Clusters for K_2MX_4 Type Solids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 343:1, 133-138

To link to this article: http://dx.doi.org/10.1080/10587250008023515

Mol. Cryst. and Liq. Cryst., 2000, Vol. 343, pp. 133-138
Reprints available directly from the publisher
Photocopying permitted by license only

Theoretical Study of the Antiferromagnetic Model Clusters for K_2MX_4 Type Solids

TAKU ONISHI, TOMOHISA SODA, YASUTAKA KITAGAWA, YU TAKANO, DAISUKE YAMAKI, SATOSHI TAKAMIZAWA, YASUNORI YOSHIOKA and KIZASHI YAMAGUCHI

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560–0043, Japan

Magnetic properties for the K_2MX_4 type solids (M=Cu^{2+}, Ni^{2+} X=F^-, O^{2-}, Cl^-) were investigated by the *ab initio* calculations using UHF and the hybrid Density Functional methods (B2VWN, S2VWN and UB3LYP). It was found that these type solids had the antiferromagnetic interactions.

Keywords: the K_2MX_4type solids; effective exchange integrals (J_{ab}); antiferromagnetic; Density Functional methods

INTRODUCTION

It is known that the K_2MX_4type solids are usually antiferromagnetic. In the previous study [1, 2], the M-X-M and the X_3M-X-MX_3 systems were investigated as the models of the solids. As a continuation of previous work, we here investigate the linear chain and the square planar clusters. Computational methods employed here are the unrestricted Hartree Fock method (UHF), the hybrid Density Functional methods (B2VWN, S2VWN and UB3LYP) and the UHF Møller Plesset perturbation method

(UMP2)[3]. The effective exchange integrals (J_{ab})[4,5] for the linear models are calculated using the energy difference between the highest and lowest spin states as shown previously [6,7]. MINI with Hay's Diffuse is used for the all metals and 6-31G* is used for X as the basic functions.

THEORETICAL BACKGROUNDS

The broken-symmetry wavefunctions are often used for calculations of the effective exchange integrals (J_{ab}) of the Heisenberg model. Previously we have derived a general formula for J_{ab} of the linear uniform chair as shown in Figure1(**A**). Here, a general formula for the ring with uniform J_{ab} is first derived using the approximate spin projection procedure. The Heisenberg Hamiltonian for the ring as shown in Figure1 (**B**) is given by

$$\hat{H}(HB) = -2J_{ab}\sum_{i=1}^{n}\mathbf{s}_i \bullet \mathbf{s}_j \ \{j = i+1 (i \neq n) \text{ and } j = 1 (i = n)\} \tag{1a}$$

$$= -J_{ab}[\mathbf{S}^2 - \sum \mathbf{s}_i{}^2 - X] \tag{1b}$$

$$X = \sum_{j,k} \mathbf{s}_j \bullet \mathbf{s}_k \ (\mathrm{j,k} \in \text{non nearest neighbor(NN)}, \mathrm{j} \neq \mathrm{k}) \tag{1c}$$

where **S** is the total spin operator, while $\mathbf{s}_i$ denotes that of the i-site spin.

$$\mathbf{S} = \sum_{i=1}^{n} \mathbf{s}_i \tag{2}$$

Then we can obtain the expectation values of H(HB) for the highest-spin (HS) state and the lowest-spin (LS) state.

$${}^{LS}\langle H\rangle = -J_{ab}[{}^{LS}\langle \mathbf{S}^2\rangle - n\langle \mathbf{s}_i{}^2\rangle - {}^{LS}\langle X\rangle] \tag{3a}$$

$$^{HS}\langle H\rangle = -J_{ab}[^{HS}\langle \mathbf{S}^2\rangle - n\langle \mathbf{s}_i^2\rangle - ^{HS}\langle X\rangle] \tag{3b}$$

Assuming the expectation value of non-NN spin coupling operator to be either $\langle\uparrow\uparrow\rangle$ or $\langle\uparrow\downarrow\rangle$, we can evolute <X> terms for the 2n-site ring model.

$$^{LS}\langle X\rangle = 2n(n-1)\langle\uparrow\uparrow\rangle + 2n(n-2)\langle\uparrow\downarrow\rangle \tag{4a}$$

$$^{HS}\langle X\rangle = 2n(n-1)\langle\uparrow\uparrow\rangle + 2n(n-2)\langle\uparrow\uparrow\rangle \tag{4b}$$

Subtracting Eq. (3b) from Eq. (3a) and substituting Eq. (4a) and (4b) for <X> terms, we obtain

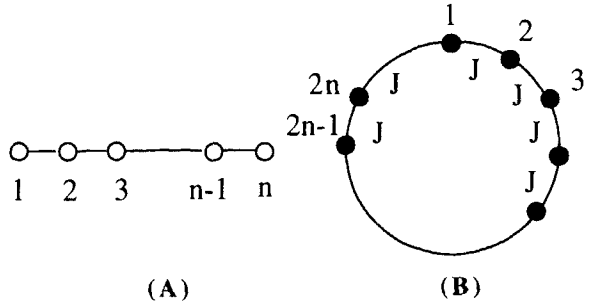
$$^{LS}\langle H\rangle - ^{HS}\langle H\rangle = J_{ab}[^{HS}\langle \mathbf{S}^2\rangle - ^{LS}\langle \mathbf{S}^2\rangle - 2n(n-2)\{\langle\uparrow\uparrow\rangle - \langle\uparrow\downarrow\rangle\}] \tag{5}$$

Instantly

$$J_{ab} = \frac{^{LS}\langle H\rangle - ^{HS}\langle H\rangle}{^{HS}\langle \mathbf{S}^2\rangle - ^{LS}\langle \mathbf{S}^2\rangle - 2n(n-2)\{\langle\uparrow\uparrow\rangle - \langle\uparrow\downarrow\rangle\}} \tag{6}$$

For the four-site ring model (n=2), which is the special case

$$J_{ab} = \frac{^{LS}\langle H\rangle - ^{HS}\langle H\rangle}{^{HS}\langle \mathbf{S}^2\rangle - ^{LS}\langle \mathbf{S}^2\rangle} \tag{7}$$

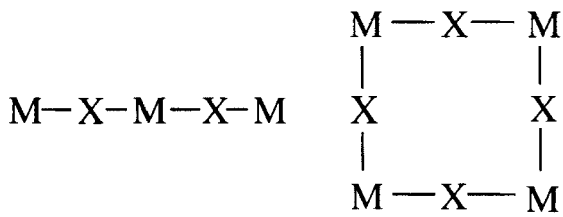


(A) (B)

FIGURE 1

NUMERICAL RESULTS AND DISCUSSION

As shown in Figure2, we have examined the linear trimer M-X-M-X-M (**1**) and the square planar X_4M_4 (**2**) as the simplest examples of the linear clusters and the square clusters, respectively. The J_{ab} values of the Cu-F-Cu-F-Cu (**1a**) system and Cu_4F_4 (**2a**) system are shown in TABLE 1 and those of Ni-F-Ni-F-Ni (**1b**) system and Ni_4F_4 (**2b**) system in TABLE 2. These values are obtained at the most energetically stable distances. The J_{ab} values of K_2CuF_4 and K_2NiF_4 solids have been determined by several experimental techniques[8]. Therefore, we compare the calculated J_{ab} values with the experimental ones. The model clusters exhibit the antiferromagnatic interactions, in accord with the experiments. Since the UHF method does not include the effect of the electronic correlation, the calculated $|J_{ab}|$ value is too small as compared with the experimental value. B2VWN and S2VWN, which are the hybrid DFT methods, have provided reliable values. On the other hand, the $|J_{ab}|$ values are overestimated in the UB3LYP method. It is because the B3LYP parametrization is appropriate for stable molecules at equilibrium geometries.



(**1**) (**2**)

FIGURE 2 Model clusters for computations

CONCLUDING REMARKS

UHF, UMP2 and DFT(UB2VWN, US2VWN andUB3LYP)calculations were performed in order to elucidate the effective exchange interactions (J_{ab}) between metal ions. The J_{ab} values obtained by calculations are consistent with the experimental values, especially in the Hybrid DFT. It is found that we can apply obtaining the effective exchange intagrals to the ring models.

TABLE1 The calculated J_{ab} values for Cu-F-Cu-F-Cu and Cu_4F_4

Structure	Methods	M-X[a)]	J_{ab}[b)]	J_{ab}(obs)[b)]
Cu_3F_2	UHF	1.92	-40.3	
(1a)	UMP2	1.92	-234.3	
	UB2VWN	1.90	-135.8	
	US2VWN	1.86	-154.0	
	UB3LYP	1.91	-441.0	
Cu_4F_4	UHF	1.89	-47.1	-132.0
(2a)	UMP2	1.90	-97.1	
	UB2VWN	1.89	-176.2	
	US2VWN	1.85	-198.6	
	UB3LYP	1.89	-573.9	

a)Å b)cm^{-1}

TABLE2 The calculated J_{ab} values for Ni-F-Ni-F-Ni and Ni_4F_4

Structure	Methods	M-X[a)]	J_{ab}[b)]	J_{ab}(obs)[b)]
Ni_3F_2	UHF	1.94	-7.14	
(1b)	UMP2	1.95	-11.1	
	UB2VWN	1.94	-24.0	
	US2VWN	1.89	-31.2	
	UB3LYP	1.94	-72.0	
Ni_4F_4	UHF	1.92	-8.68	-36.0
(2b)	UB2VWN	1.91	-32.5	
	US2VWN	1.87	-43.9	
	UB3LYP	1.91	-92.4	

a)Å b)cm^{-1}

ACKNOWLEDGEMENTS

This work has been supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 10132241 and No. 10149105) from the Ministry of Education, Science, Sports and Culture, Japan.

References

[1] M. Fujiwara, M. Nishino, S. Takamizawa, W. Mori and K. Yamaguchi, *Mol. Cryst. Liq. Cryst.*, **286,** 185(1996).
[2] K. Yamaguchi, T. Takahara, T. Fueno, and K. Nasu, *Jpn. J. Appl. Phys.*, **26,** L1362(1987).
[3] Gaussian 94, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Oritiz, J. B. Foresman, J. Cioslowski, B. B.Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Repłogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
[4] T. Kawakami, S. Yamanaka, Y. Takano, Y. Yoshioka and K. Yamaguchi, *Bull. Chem. Soc. Jpn.*, **71,** 2097 (1998).
[5] S. Yamanaka, T. Kawakami, S. Yamada, H. Nagao, M. Nakano and K. Yamaguchi, *Chem. Phys. Lett.*, **240,** 268 (1995).
[6] K. Yamaguchi, T. Tsunekawa, Y. Toyoda and T. Fueno, *Chem. Phys. Lett.*, **143,** 371 (1988).
[7] M. Nishino, Y. Yoshioka and K. Yamaguchi. *Chem. Phys. Lett.* **297,** 51 (1998).
[8] G. Shirane, Y. Endoh, R.J. Birgeneau, M.A. Kastner, Y. Hidaka, M. Oda, M. Suzuki and T. Murakami, *Phys. Rev. Lett.*, **59,** 1613 (1987).