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Theoretical Calculations of Magnetic Interactions in Frustrated Antiferromagnetic Cluster

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Inter-dimer magnetic interactions ($J_{ab(D)}$) between (BEDT-TTF)$_2^+\bullet$ dimers in the κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ crystal has been studied theoretically. In these crystals, triangular lattice structure with spin frustration has been discovered and experimental studies have been performed by several research groups. We have calculated the inter-dimer $J_{ab(D)}$ values by using several methods. In addition, we have analyzed the spin lattice with optimization of θ angle in classical Heisenberg spin model and with numerical diagonalization in quantum Heisenberg spin model.

Keywords: BEC; DFT; effective exchange integral; organic superconductor; spin frustration; spin liquid

INTRODUCTION

Triangle spin structures play important roles in exchange-forbidden free-radical reactions [1,2] as well as in spin frustration of quantum spins [3]. Anderson has emphasized that the resonating valence-bond

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(RVB) model is a first step to understand the nature of high-T_c superconductivity [4]. Recently, several research groups have reported the spin frustration behaviour in molecular crystals [l–4]. Such spin frustration will be deduced from triangle geometry. First in the field of molecular magnetism, Awaga and his co-workers reported that m-MPYNN$^+$(ClO_4^-)$_{0.72}I^-_{0.28}$ crystal had spin fluctuation, about a decade ago [5,6]. Very recently, Kanoda, Saito and their co-workers reported κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ (**1**) crystal [7,8]. Tamura, Kato and their co-workers reported β'-Me$_4$P[Pd(dmit)$_2$]$_2$ crystal [9–12]. In this paper, we will consider only crystal **1** in order to investigate spin frustration problem in relation to the superconductivity.

CRYSTAL MOLECULAR STRUCTURES

We have treated the crystal **1** to study spin frustration, which has been one of the most interesting crystals by many scientists now. First, we illustrate the crystal structure of **1** at the temperature of 295 K in Figure 1A [8]. We can find alternative stacking of both BEDT-TTF layers and counter layers [7,8]. Arrangement of BEDT-TTF molecules in their layer is depicted in Figure 1B as view of a-axis. Especially, the two molecules contact each other with close face-to-face type stacking and realize dimer structure. Such dimers suffer charge transfer of one hole from their counter ions and get one radical spin per one dimer. This structure is similar to crystalline structure of the κ-phase BEDT-TTF and BETS salts, which have been treated in our previous calculations [13–17].

THEORETICAL CALCULATIONS

Evaluation of Inter-dimer $J_{ab(D)}$ Values

In series of our studies [13–17], effective exchange integrals (J_{ab}) successfully describe magnetic interaction. The magnetic interaction between localized electrons is usually described by the Heisenberg-type spin coupling Hamiltonian [1,2,18–20]. Our broken-symmetry (BS) MO approach [21,22] coupled with the Heisenberg model can evaluate J_{ab} values directly. We have proposed computational schemes of the inter-dimer magnetic interaction ($J_{ab(D)}$): (1) indirect evaluation from inter-molecule J_{ab} values ($J_{ab(M)}$) with approximate equation: $J_{ab(D)} = J_{ab(M)}/2$ ($\mathbf{M}^{+\cdot} - \cdot\mathbf{M}^{+}$). (2) direct evaluation in cluster of four molecules with two holes ((**M**-**M**)$^{+\cdot}$ – ·(**M**-**M**)$^+$). Suitable spin structure and localization/delocalization of spin densities have been essential to obtain the reasonable SCF solutions with the good

convergence. Our calculations have been carried out by the UB3LYP/6-31G method in Gaussian 98 program packages [23].

For cluster systems of BEDT-TTF dimers, all the evaluated $J_{ab(D)}$ values are also shown in Figure 1B. Symmetrical operation duplicates the dimers each other and one identical relation is found. Magnetic interaction between $(BEDT\text{-}TTF)^{+}$**.**s within one dimer is very strong ($-594\,cm^{-1}$) and therefore dimer structure can be accepted. For the $J_{ab(D)}$ values by scheme (1), three dimers are interacted with almost equal antiferromagnetic spin coupling (-52 (J_1) cm^{-1}, -51 and -51 (J_2) cm^{-1}) and spin frustration in regular triangle magnetic structure may occur. For the $J_{ab(D)}$ values by scheme (2), spin structure of isosceles triangle type is found (-20 (J_1) cm^{-1}, -33 and -33 (J_2) cm^{-1}). Though we only extracted three dimers from whole BEDT-TTF layer, two dimensional spin networks based on these spin couplings spread in T-shape contact of $(BEDT\text{-}TTF)_2^{+}$• units.

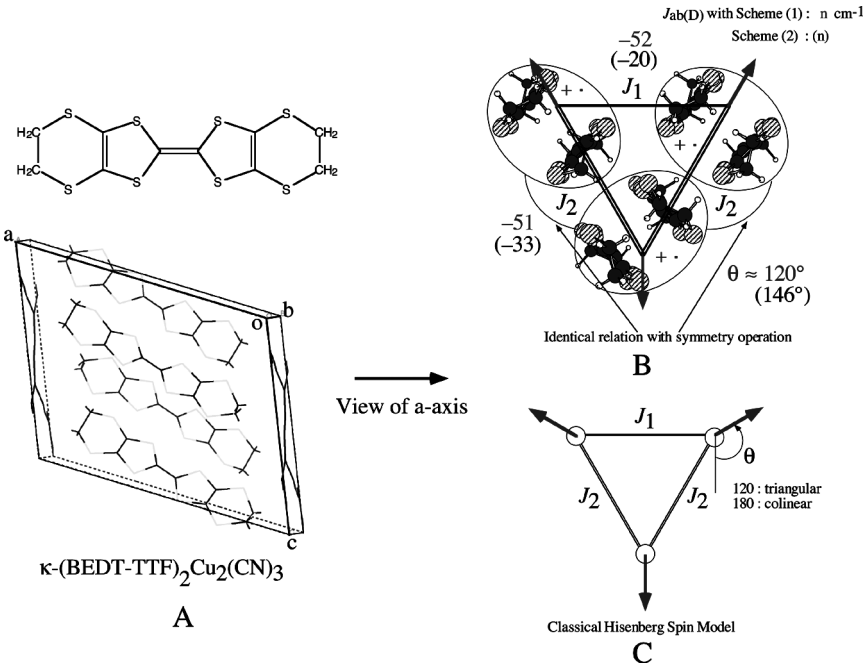

FIGURE 1 (A) Crystal structure of κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ (**1**). (B) The evaluated $J_{ab(M)}$ values between $(BEDT\text{-}TTF)_2^{+}$**.** dimers and the minimized θ values be using of computational schemes (1) and (2). (C) Definition of classical Heisenberg spin model for simple isosceles triangle structure.

POSSIBLE PHASE DIAGRAMS

Noncollinear Spin Structure with Classical Heisenberg Spin Model

The most stable spin orientation in the long-range classical order can be calculated easily with classical Heisenberg spin model. Simple model of isosceles triangle with only J_1 and J_2 parameters are illustrated in Figure 1C. Angle parameter θ is defined as the twist angle between two spin vectors, and the cases with $\theta = 120^\circ$ and 180 indicate regular triangle and collinear spin structure, respectively. The classical Heisenberg spin Hamiltonian is defined [2] as

$$H(CHB) = J_1 S^2 \cos(2\pi - 2\theta) + 2J_2 S^2 \cos\theta \qquad (1)$$

and S = 1/2. We calculated the suitable θ values, which minimized the total energy.

The optimized θ values are about 120° and 146°. Therefore spin vectors in exact and near regular triangle are expected for the computational schemes (1) and (2), respectively as also illustrated in Figure 1B.

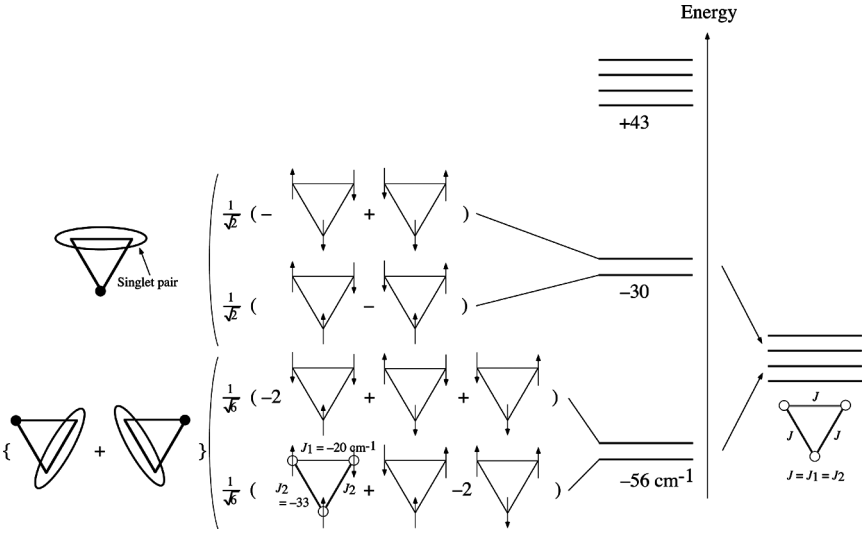

FIGURE 2 Numerical diagonalization of Heisenberg Hamiltonian for quantum spin lattice.

Numerical Diagonalization of Heisenberg Hamiltonian for Quantum Spin Lattice

In order to study quantum spin liquid state the numerical diagonalizating procedure [l] for Heisenberg Hamiltonian is very efficient. The matrix $(2^N * 2^N)$ defined as

$$H_{nm} = \left\langle n \middle| -2\sum_{ij} J_{ij}\mathbf{s}_i \cdot \mathbf{s}_j \middle| m \right\rangle \quad (n, m\text{: spin configuration}; i, j\text{: spin sites}) \tag{2}$$

can describe the quantum spin lattice (N: number of spin sites). First, we applied our scheme to triangle spin lattice ($N = 3$) as the minimum

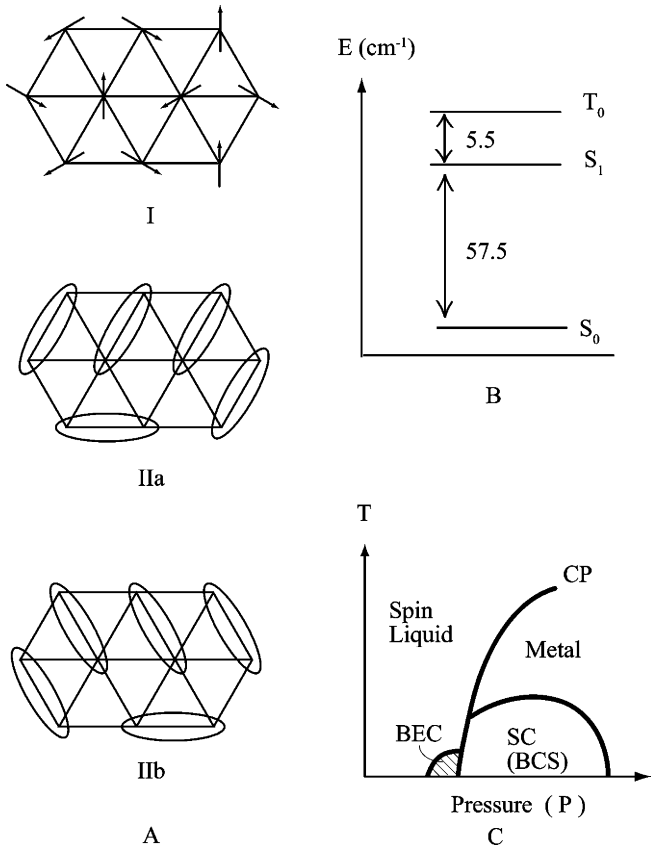

FIGURE 3 Classical (I) and RVB (IIa, IIb) structures (A), energy levels (B) and possible phase diagram (C) for **1**. CP means the critical point.

system [l,2]. Each J value is set to be $J_1 = -20$, $J_2 = -33$ as evaluated with the scheme (2). From the obtained numerical results with our program package [24], eigen values and eigen vectors were evaluated as shown in Figure 2. The ground state is doublet and first excited state is also doublet. If the system of $J_1 \approx J_2$ (scheme (1)) is realized, it is expected that two double states degenerate and turn to be the so-called resonating valence-bond (RVB) state [3,4]. The VB structures [l] are also illustrated in this figure.

DISCUSSION AND CONCLUDING REMARKS

The exact diagonalization often $S = 1/2$ spins with the J-values by scheme (1) have been performed to elucidate classical spin and RVB structures, energy level, and possible phase diagram. The triangular lattice (I) is realized under the classical HB model [2], while the singlet pair (IIa, IIb) is predicted by the quantum HB model [2–4] (See Fig. 3A). The energy gap between the ground singlet and excited triplet states is about $63\,cm^{-1}$ as shown in Figure 3B, showing the nonmagnetic spin liquid state, in agreement with the experiment [7]. Judging from the available experiments [7], the Bose-Einstein condensation (BEC) of singlet pair (boson), namely quantum long-range order, may be realized at a very low temperature in stead of the classical Neel order. The BEC-BCS crossover by the external pressure would be an interesting problem as illustrated in Figure 3C [25].

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