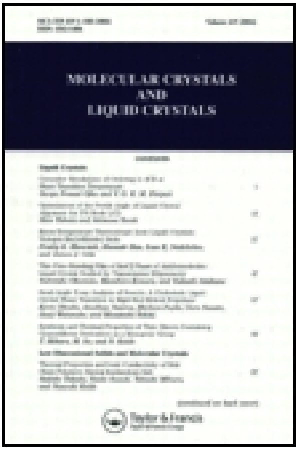

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Spin-Polarized Band Sturcture for Organic Molecular Crystals

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SPIN-POLARIZED BAND STURCTURE FOR ORGANIC MOLECULAR CRYSTALS

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Abstract We carry out full-potential LAPW (FLAPW) band calculations for ferromagnetic states of the hypothetical square lattices of H_2NO chains by assuming two kinds of stacking of H_2NO molecules: (A) face-to-face stacking and (B) anti-phase alternating stacking. In the case (A), the ferromagnetic state has not been obtained as a stable state. In the case (B), on the other hand, the metallic ferromagnetic state has been obtained certainly as a stable state. For the intra-chain molecular distance λ=2.25 Å, the obtained spin moment is $m_s = 0.45\ \mu_B$/molecule.

INTRODUCTION

In recent decades much interest has been paid to molecular magnetism, in particular to systhesizing organic ferromagnets, and quite recently bulk ferromagnetism has been confirmed in several purely organic materials.[1–3] But their transition tempratures are quite low in comparison to transition metal magnets. Most of the ferromagnetic or antiferromagnetic molecular crystals thus far discovered are well described in terms of Heisenberg Hamiltonian of localized S=1/2 spins. The exchange coupling J has been discussed mainly in the framework of intermolecular charge transfer interaction based on McConnel model[4], and it has been clarified that the sign of J can be positive (ferromagnetic) if the transfer between SOMO's is smaller compared with that between SOMO and NHOMO (or NLUMO). Low T_c is ascribed to small magnitude of J. Generally speaking, in 3d magnetic systems ferromagnets with quite high T_c are realized in metallic systems. Then we expect that much higher T_c would be obtained by synthesizing metallic organic ferromagnets.

In our previous work,[5] we have determined the magnetic phase diagram of the extended Hubbard system in which each molecule has two different orbitals by investigating the instability of paramagnetic phase within the HF-RPA approximation. The result shows the metallic ferromagnetism may be realized when electron filling is 1/4 (or 3/4) and if the transfer between the different orbitals is much larger than that between the same orbitals. We have carried out also full-potential LAPW (FLAPW) band calculations for the paramagnetic states of hypothetical square lattices of H_2NO chains by assuming two kinds of stacking of H_2NO molecules: (A) face-to-face stacking and (B) anti-phase alternating stacking.[6] The calculated band structure of the case (B) seems to satisfy the condition for ferromagnetism obtained by us in Ref. 5. In the case (A), on the other hand, there is a possibility of an antiferromagnetic state, but a ferromagnetic state seems hard to be realized. Quantum chemical calculation of exchange interaction between two H_2NO molecules by Yamaguchi *et al.*[7] is consistent with this result.

In this paper we carry out FLAPW band calculations for ferromagnetic states of the hypothetical square lattices of H_2NO chains.

BAND CALCULATIONAL PROCEDURE

For the H_2NO chain we consider two kinds of stacking of H_2NO molecules as shown in Figure 1: (A) face-to-face stacking and (B) anti-phase alternating stacking. The former corresponds to the syn-dimer and the latter to the anti-dimer. For the atomic distance within a H_2NO molecule we use 1.04 Å for N-H and 1.23 Å for N-O, and the angle of H-N-H is taken to be 120°.[8] The lattice constant b of the square lattice has been fixed as 4.0 Å. The value of the intra-chain molecular distance λ has been varied from 2.25 Å to 3.0 Å for the case (A)(to 3.5 Å for the case (B)) with an interval 0.25 Å.

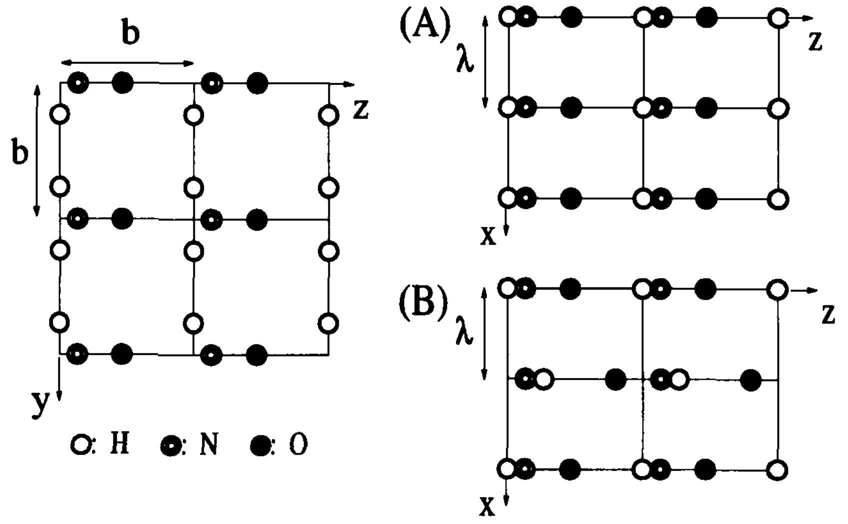

FIGURE 1 Two types of hypothetical sturucture of H_2NO crystal.

Our band calculations are based on a scalar-relativistic version of the full potential linearized APW (FLAPW) method, *i.e.* relativistic effects other than the spin-orbit interaction are included. We introduce practically the muffin-tin (MT) sphere around each atom, but the potential is determined fully self-consistently through the whole crystal (both indside and outside the MT spheres). For the exchange-correlation potential we have used the Gunnarsson-Lundqvist type.[9] The core electrons are treated as relaxed.

The basis LAPW's inside the MT sphere are expanded up to $\ell_{max}=3$, and the wave functions are expanded in terms of LAPW's up to $|G|_{max}$. Here $|G|_{max}$ represents an appropriate cut-off value for reciprocal lattice vectors G, and the number of basis functions used actually are determined by the value of $|G|_{max}$. For example, we have set $|G|_{max}$ to be 7.8 $Å^{-1}$ for $\lambda=2.75$ Å, and then the number of basis functions are about 360 (720) for the case(A) (case(B)). The potential inside the MT spheres are expanded up to $\ell_{max}=2$, while outside the MT spheres it is expanded in Fourier series of reciprocal lattice vectors up to $2 \times |G|_{max}$.

We have determined self-consistently the charge density of the crystal using eight k points in the iteration process. The density of states (D.O.S.) has been calculated with a linearly energy-interpolated tetrahedron method.

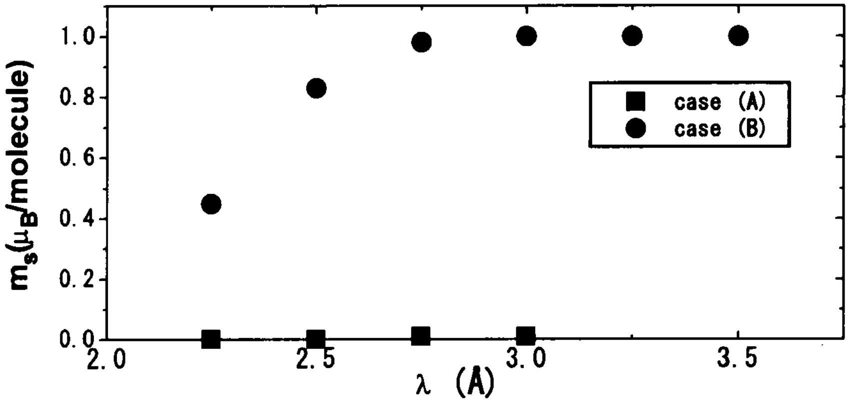

FIGURE 2 The magnetic moment per molecule, m_s, as a function of λ (intra-chain molecular distance). The filled squares represent the results for the case (A) and the filled circles those for the case (B).

SPIN MOMENT AND BAND STRUCTURE

We show in Figure 2 the spin moment per molecule, m_s, determined as a function of λ for both the cases (A) and (B). In the case (A), m_s has converged practically to 0 μ_B. It means that there is not a stable ferromagnetic state in this case.

In the case (B), on the other hand, m_s has converged certainly to finite values. For $\lambda = 2.25$ Å and 2.50 Å the value of m_s reduces significantly from 1 μ_B. In these cases the spin-up and spin-down bands of SOMO orbitals overlap considerably and both of them cross the Fermi level, *i.e.* a metallic ferromagnetic state is realized.

For $\lambda = 3.00$ Å, 3.25 Å and 3.50 Å, on the other hand, the exchange splitting of the SOMO band is large enough to make a gap between the minority and the majority spin bands (*i.e.* insulating ferromagnetic state). As the results we have $m_s = 1$ μ_B.

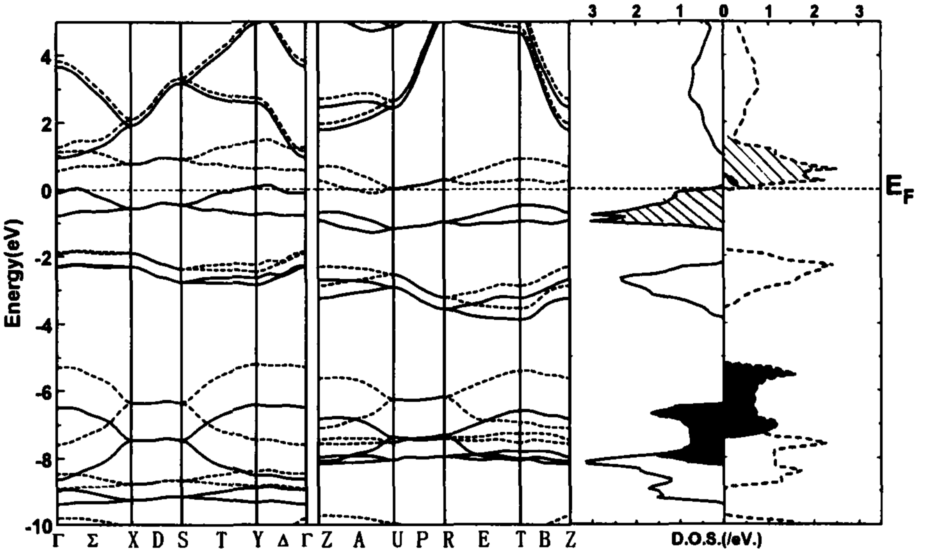

FIGURE 3 The energy dispersion curves and the electronic D.O.S. for $\lambda = 2.75$ Å in the case (B). Majority and minority spin band are shown by the solid and dashed curves, respectively. The hatched region denotes the band arising from the anti-bonding states of the π-orbitals of N and O (SOMO band), whereas the shaded region that arising from the bonding states (3rd HOMO band).

The case of $\lambda = 2.75$ Å seems to be just the boundary between the metallic and insulating ferromagnetic states (see Figure 3 which shows the energy dispersion curves and the D.O.S. for $\lambda = 2.75$ Å).

As seen from the D.O.S. in Figure 3, large exchange splitting is seen only in the hatched and the shaded regions. The hatched region corresponds to the anti-bonding states of the π-orbitals of N and O (SOMO band) and the shaded region to the bonding states (3rd HOMO band). Therefore we can say it is these two orbitals, bonding and anti-bonding π-orbitals of N and O, that play important roles in realizing the ferromagnetic state. Thus the present system seems to be well described by a $\frac{3}{4}$-filling two-band Hubbard model in our previous work.[5]

In conclusion, the calculational results of spin polarized band structures of the hypothetical square lattices of H_2NO chains are summarized as follows:

(A) Face-to-face stacking of H_2NO molecules:
The magnetic moment has converged to zero, *i.e.* the ferromagnetic state has not been obtained as a stable state as expected from the result of band calculations for the paramagnetic state.

(B) Anti-phase alternating stacking of H_2NO molecules:
The ferromagetnic state has been obtained certainly as a stable state. In the case of $\lambda < 2.75$ Å a ferromagentic metallic state is realized and the spin moment per molecule is reduced significantly from 1 μ_B, *e.g.* $m_s = 0.45\ \mu_B$ when $\lambda = 2.25$ Å. In the case of $\lambda > 2.75$ Å, on the other hand, a complete ferromagentic state (insulating state) is realized, *i.e.* the minority and the majority spin bands of SOMO states split completely. The present result is the first example which shows an existence of a stable metallic ferromagnetic state in purely organic systems.

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