First-Principles Study of the Ferromagnetic and Semiconductor Properties of [Mn(4,4′-bipy)(N₃)₂]ₙ

J.W. Li¹, G.Y. Gao², and F. Jia³

¹Department of Physics, Nanchang Institute of Technology, Nanchang 330099, China
²Department of Physics, Huazhong University of Science and Technology, Wuhan 430074, China
³Department of Physics, Jiangxi Normal University, Nanchang 330022, China

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Based on density functional theory, the full potential linearized augmented plane wave (FPLAPW) method is applied to study the electronic structure and the magnetic properties of the compound [Mn(4,4′-bipy)(N₃)₂]ₙ. The density of states, the spin magnetic moment and the electronic band structure are calculated. The results indicate that the compound has ferromagnetic and semiconductor properties. It is found that there is hybridization between the d orbital of the central Mn atom and the p orbital of the N atom, and that there exists a spin delocalization from the Mn atom towards the N atoms of the EE-azide groups. Through the EE-azide bridges, the spin delocalization makes the neighboring Mn atoms having a dominant ferromagnetic interaction. The magnetic moment 5.0 µB per molecule mainly comes from Mn ion with little contribution from the EE-azide groups.

Keywords: FPLAPW; Electronic structure; Ferromagnetic; Semiconductor

I. INTRODUCTION

In the past decades, the molecular-based magnetic materials with paramagnetic metal ions, where the bridging ligands act as a super-exchange pathway between the metal centers, have been considerably studied both experimentally and theoretically, and some new materials have also been synthesized [1-5]. Recently the investigation of organic magnetic materials containing only light elements, typically C, H, O, N and S, has been drawn more and more attention [6-11]. Pure organic magnetic materials have free radicals, which can supply the magnetic moment, but generally their transition temperatures are too low for practical applications. The synthesis of the molecular-based ferromagnet with metallic ions has attracted an extensive interest. The solid-state assembly of metal-organic polymers has also the potential applications in nonlinear optics, magnetism and molecular recognition.

The compound [Mn(4,4′-bipy)(N₃)₂]ₙ consists of a 3D network in which Mn(II) cations are octahedrally coordinated to six N-atoms: four of them corresponding to single EE azides, on the equatorial positions, and two of them to 4,4′-bipy ligands, on the axial ones [12,13]. The structure is rather complex as the six ligands connected to each metal ion perform as intermetallic bridges. The pseudohalide ligands provide a tetrahedral topology around Mn(II) cations resulting in an azide-linked diamondoid network, which have been recognized as potential structural motifs for the construction of acenitic solids. The singularity of the compound lies on the absence of a center of symmetry that is a requirement for many bulk properties of solid materials. The structure of the compound which should be useful for the design of novel molecular-based ferromagnet with metallic ions. Our results show that there exists a dominant ferromagnetic interaction arises from the EE-azide groups part of the compound. In addition, we find that the spin magnetic moment mainly comes from Mn ion, and there are smaller positive spin populations on the EE-azide groups. This paper is organized as follows. In Section 2 we present the computational method. Section 3 is devoted to the results and discussions. Finally, we summarize the results in Section 4.

II. COMPUTATIONAL METHODS

The calculations presented in this work are performed by employing the first principles full potential linearized augmented plane wave (FPLAPW) method, which is among the
most accurate band structure methods presently available and has been applied to materials simulation successfully. In this method, no shape approximation is used for either the potential or the electronic charge density. We use the wien2k [14] package that allows inclusion of local orbitals in the basis, which upon linearization improves and makes possible a consistent treatment of semi-core and valence in one energy window. In general, the local density approximation (LDA) and the generalized gradient approximation (GGA) can be chosen in wien2k code. Considering the success of the GGA derived from their ability to correct some LDA deficiencies with a modest increase in computational workload, the GGA is mandatory for systems containing "weak" or hydrogen bonds such as molecular crystals; for these systems the intermolecular bond lengths are severely underestimated in LDA, but they can be appreciably improved in GGA. In addition, the GGA has been demonstrated to be capable of calculating organic magnets [15]. So in our calculations, the exchange and correlation effects are treated with the GGA according to Perdew et al [16].

The compound \([\text{Mn}(4,4′\text{-bipy})(\text{N}_3)_{2}]_n\) crystallizes in the tetragonal system, space group is P43212. There are four molecules in one primitive cell, as shown in Fig. 2. For clear view, we only label the hydrogen atom in part. The structure parameters of the compound are \(a=8.229(2)\,\text{Å},\, b=8.229(2)\,\text{Å},\, c=16.915(7)\,\text{Å}\). The atomic-sphere radii \(R_{\text{mt}}\) are chosen as 2.18, 1.08, 1.13 and 0.61 a.u. for Mn, N, C and H, respectively. We set the charge density Fourier expansion up to \(l=10\) and the charge density Fourier expansion cutoff \(G_{\text{max}}=14\) in the muffin-tins. One hundred \(k\)-points in the first Brillouin zone are adopted in the calculations. The plane wave cutoff energy is 146 eV. In order to achieve a satisfactory degree of convergence, the cutoff parameter is taken to be \(R_{\text{mt}}K_{\text{max}}=2.0\), where \(K_{\text{max}}\) is the maximal value of the reciprocal lattice vector used in the plane wave expansion, and \(R_{\text{mt}}\) is the smallest atomic sphere radius in the unit cell. The self-consistency calculations are considered to be converged only when the energy difference between input and output energy is less than \(10^{-5}\) Ryd per formula unit.

![FIG. 2: ORTEP labeled primitive cell for \([\text{Mn}(4,4′\text{-bipy})(\text{N}_3)_{2}]_n\).](image)

(For clarity we only label the hydrogen atom in part.)

III. RESULTS AND DISCUSSION

In order to study the electronic structure and the magnetic properties of \([\text{Mn}(4,4′\text{-bipy})(\text{N}_3)_{2}]_n\), the total DOS of the molecule, the total DOS of Mn, N3, N4, N5 are calculated as shown in Fig. 3. Because the DOS distribution near the Fermi level determines the magnetic properties, we concentrate our attention on the DOS distribution from -6 to 2 eV. In the vicinity of the Fermi level, we find that the total DOS distribution of the up- and down-spin electrons is obviously split. These energy bands are decomposed into two subbands: one is the up-spin valence band; the other is the down-spin band. Thus the ordered spin arrangement of electrons is formed by the exchange correlation of electrons, which provides the static magnetic moment of this compound. According to the DOS distribution, it is worthwhile to note that the main origin of magnetism is provided by Mn atom, in addition, the N3, N4 and N5 atoms also contribute to the spin magnetic moment, and the net spin of Mn is parallel to those of N3, N4 and N5. These phenomena play an important role in the indirect interaction between Mn(II) ions, which implies that the four EE-azide ligands act as super-exchange pathway. It is more interesting that near the Fermi level, the top of the occupied spin-up band is 1.0 eV below the Fermi level. There is an energy gap of 1.17 eV between the spin-up occupied subband and the down-spin band. Thus the compound has semiconductor properties.

![FIG. 3: DOS of the molecule and Mn, N3, N4, N5 atoms (solid: spin-up states; dotted: spin-down states. The Fermi level is located at 0 eV).](image)
TABLE I: Atomic spin magnetic moments of [Mn(4,4′-bipy)(N₃)₂]ₙ

<table>
<thead>
<tr>
<th>Site</th>
<th>Magnetic moment (µ_B)</th>
<th>Site</th>
<th>Magnetic moment (µ_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn1</td>
<td>4.31100</td>
<td>C2</td>
<td>0.00033</td>
</tr>
<tr>
<td>N1</td>
<td>0.00858</td>
<td>H2</td>
<td>0.00007</td>
</tr>
<tr>
<td>N2</td>
<td>0.00888</td>
<td>C3</td>
<td>0.00139</td>
</tr>
<tr>
<td>N3</td>
<td>0.02145</td>
<td>C4</td>
<td>0.00094</td>
</tr>
<tr>
<td>N4</td>
<td>0.01148</td>
<td>C5</td>
<td>0.00050</td>
</tr>
<tr>
<td>N5</td>
<td>0.02043</td>
<td>H5</td>
<td>0.00007</td>
</tr>
<tr>
<td>C1</td>
<td>0.00261</td>
<td>C6</td>
<td>0.00211</td>
</tr>
<tr>
<td>H1</td>
<td>0.00004</td>
<td>H6</td>
<td>0.00005</td>
</tr>
</tbody>
</table>

spin delocalization from the Mn atom towards the two 4,4′-bipy ligands is weak. That is to say, the ferromagnetic interaction mainly arises from the four EE-azide bridges. In the present calculations, the spin magnetic moment of the unit cell is 20.004 µ_B. Because there are four molecules in one primitive cell, the spontaneous magnetic moment of the molecule is about 5.001 µ_B per molecule. The Mn²⁺ ion with 3d⁵ has five unpaired electron, therefore our calculations is reasonable. In the FPLAPW method, the unit cell is divided into two parts: (1) non-overlapping atomic spheres (centered at the atomic sites) and (2) an interstitial region. The magnetic moments of atoms add up to a saturation moment of 4.390 µ_B per molecule, and the interstitial moment yields the remaining 0.699 µ_B per molecule.

To exploit the mechanism of the magnetic interactions in Mn(4,4′-bipy)(N₃)₂ₙ, the partial density of states of Mn d, N₃ p, N₄ P and N₅ p is shown in Fig. 4. It is quite obvious that the total atomic DOS comes nearly only from d orbitals of Mn and p orbitals of N₃, N₄, N₅ in the energy range. In addition, the partial DOS of Mn d, N₃ p, N₄ P and N₅ p below the Fermi level have similar peaks and character, which indicates that there exist hybridizations between Mn d and N₃ p, N₄ P and N₅ p. It is worthwhile to say that the hybridizations reveals two points: (i) the four orbitals are strongly mixed over the energy region which means the N₃ P orbital, N₄ P orbital and the N₅ P orbital are responsible for the magnetic coupling in the molecule, and the strong overlap of the magnetic orbitals below the Fermi level between Mn and the four EE-azide ligands that link the manganese centers indicates the contribution of the super-exchange interaction to the magnetism and (ii) the net spin of Mn d is parallel to those of N₃ p, N₄ P and N₅ p, so the ordered spin arrangement is formed by the super-exchange interaction.

For further consideration, we also give the electronic band structure in Fig. 5 (solid line is the spin-up electronic band; dashed line is the spin-down electronic band). As shown in Fig. 5, the spin-up electronic bands are below the Fermi level, but the spin-down electronic bands are above the Fermi level. This means that there exists a ferromagnetic interaction between the molecules. Furthermore, we can see that the top of the spin-up occupied bands is 1.0 eV below the Fermi level and there is an energy gap of 1.17 eV between the spin-up occupied bands and the spin-up unoccupied bands, which implies that the complex has the properties of a semiconductor.

IV. CONCLUSIONS

The magnetic and the semiconductor properties have been studied by employing the FPLAPW within the framework of density functional theory for the compound [Mn(4,4′-bipy)(N₃)₂ₙ]. The results show that the compound has ferromagnetic and semiconductor properties at low temperature. The analysis of the DOS and the electronic band structure reveals that the spin magnetic moment is 5.0µ_B per molecule and the magnetic moment is mainly from the Mn ion and a little contribution from the EE-azide groups. It is also found that there exists a dominant ferromagnetic interaction arising from the EE-azide groups part of the compound.
Acknowledgments

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