

First-principles studies on the spin distribution on the dihalide-bridged polymer antiferromagnet: $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu, Fe}$)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 3325

(<http://iopscience.iop.org/0953-8984/18/12/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 09:09

Please note that [terms and conditions apply](#).

First-principles studies on the spin distribution on the dihalide-bridged polymer antiferromagnet: $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$)

L Zhu¹, K L Yao^{1,2,3} and Z L Liu¹

¹ Department of Physics and State Key Laboratory of Laser Technology, Huazhong University of Science and Technology, Wuhan 430074, People's Republic of China

² International Center of Materials Physics, The Chinese Academy of Science, Shengyang 110015, People's Republic of China

E-mail: klyao@hust.edu.cn and wl-zl41@163.com

Received 23 August 2005

Published 9 March 2006

Online at stacks.iop.org/JPhysCM/18/3325

Abstract

First-principles calculations have been performed to study the electronic band structure and the magnetic properties for the polymeric compound of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$). The relative stability of the ground state, density of states and electronic band structure were examined. Total energy calculations reveal that the antiferromagnetic phase is a stable ground state for $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$). It is noteworthy that we predict the compound $\text{Fe}(\text{thiazole})_2\text{Cl}_2$ is a metallic antiferromagnet and has a half-metallic (HM) ferromagnetic metastable state. But the spin-up and spin-down DOS in the ferromagnetic and antiferromagnetic phases of the compounds $\text{Cu}(\text{thiazole})_2\text{Cl}_2$ and $\text{Cu}(\text{thiazole})_2\text{Br}_2$ all opened a large bandgap. The spin magnetic moments of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$) are mainly assembled at the copper and iron atoms, with a little contribution from the chlorine, bromine, nitrogen, sulfur, and carbon atoms.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The quest to develop new magnets based on molecule-based materials is a growing area of contemporary materials chemistry research. The most interesting potential of molecular materials nowadays lies in the possibility to create solids in which two or more physical

³ Author to whom any correspondence should be addressed.

properties, such as conducting, magnetic and optical ones, coexist in the same crystal lattice. This novel class of multifunctional materials should provide the unique opportunity to study the competition and mutual influence of these properties. The half-metallic magnet has attracted renewed interest recently in the search for efficient spin polarizers in spin electronics, because they have only one electronic spin channel at the Fermi energy and, therefore, may show nearly 100% spin polarization [1, 2]. Since the discovery by de Groot *et al* in 1983 [3], many half-metallic ferromagnets have been theoretically predicted and some of them, furthermore, have been confirmed experimentally. For example, HM ferromagnetism has been found in mixed valence perovskites $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [4], in ferromagnetic metallic oxides such as Fe_3O_4 [5] and CrO_2 [6], in dilute magnetic semiconductors [7, 8], and in zinc-blende structure MnSb , CrAs etc [9, 10]. However, we note that all of these HM ferromagnets are pure inorganic materials, so we may ask if HM ferromagnetic property can be found in molecule-based magnetic materials such as organic or metal–organic polymers. In our group, we have found that the first genuine organic ferromagnetic radical crystal *p*-nitrophenyl nitronyl nitroxide and the fumarate-bridged polymer $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$ are half-metallic magnets [11, 12]. Therefore, it is highly desirable to explore new excellent half-metallic molecule-based magnets. Recently, the use of organic spacers as superexchange pathways between the metal ions has been of growing interest in the field of molecular magnetism.

$\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$) are polymeric systems based on transition metal copper (II) or iron (II), thiazole (tz) and di-bridging halide ligands. Polymeric systems of Cu and Co containing thiazole (tz) and di-bridging chloro ligands have been known for some time; however, only the structure of dichlorobis(thiazole)copper (II) has previously been reported, while the study on temperature dependent susceptibility by Estes and co-workers [13] revealed that the polymers $\text{Cu}(\text{tz})_2\text{X}_2$ have characteristic features of antiferromagnetic linear chains of Heisenberg spins. The synthesis and the structural characterization of the Fe analogue, dichlorobis(thiazole)iron (II), have only recently been reported [14, 15]. The structures of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$) consist of a tetragonally elongated octahedral unit, with N-donor thiazole ligands in the axial positions. These units are equatorially linked along the *b*-axis by double dihalide bridges to form infinite linear chains, as shown in figure 1(a) for $\text{Fe}(\text{thiazole})_2\text{Cl}_2$ and figure 1(b) for $\text{Cu}(\text{thiazole})_2\text{Cl}_2$. The structural characterization of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ is similar with that of $\text{Fe}(\text{thiazole})_2\text{Cl}_2$ and $\text{Cu}(\text{thiazole})_2\text{Cl}_2$, for simplicity, we do not show the structure of $\text{Cu}(\text{thiazole})_2\text{Br}_2$. The low temperature magnetic susceptibilities of $\text{Fe}(\text{thiazole})_2\text{Cl}_2$ have been fitted to a one-dimensional Ising model with a mean field correction and found to be highly anisotropic with ferromagnetic intrachain interactions along the *b* axis and weaker antiferromagnetic interchain interactions. Variable temperature susceptibility data for $\text{Cu}(\text{thiazole})_2\text{Br}_2$ were fitted by an isotropic Heisenberg model using the relations of Bonner and Fisher [16]. Interestingly, a good fit to the data for $\text{Cu}(\text{thiazole})_2\text{Cl}_2$ was found using a model for a two dimensional Heisenberg antiferromagnetic layer; however, attempts to fit to the $\text{Cu}(\text{thiazole})_2\text{Br}_2$ data to this model were unsuccessful. To understand the origin of magnetism in these compounds, a more detailed knowledge of the electronic band structure and the magnetic properties is still required.

In this paper, our main objective is to study the magnetic properties of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$) using the *ab initio* method of the full-potential linearized augmented plane wave. The main goals of our work are to investigate the electronic structure and the magnetic coupling, and to analyse the propagation of the observed magnetic interaction via the density of states (DOS) and the electronic band structure. This provides new insights to the origin of the strong ferromagnetic coupling in these compounds, which should be useful for the design of novel ferromagnetic materials.

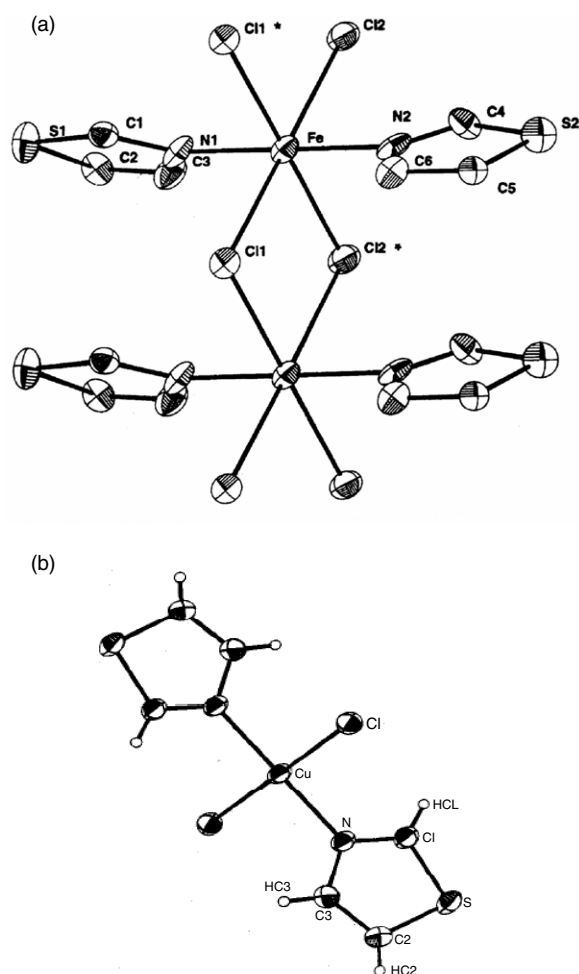


Figure 1. An ORTEP drawing of linear chains of (a) $\text{Fe}(\text{tz})_2\text{Cl}_2$ and (b) $\text{Cu}(\text{tz})_2\text{Cl}_2$. H atoms are omitted for clarity. All atoms are represented by the thermal ellipsoids with 50% probability.

2. The method and the parameters of FP-LAPW

Density functional theory (DFT) has been proved to be a powerful and economical tool for the study of a variety of molecular properties in coordination compounds [17–19]. In our calculations, the first-principles electronic structure calculations employ the well known full-potential linearized augmented plane wave (APW) method. In this method, no shape approximation either on the potential or on the electronic charge density is made. Our calculations were performed using the WIEN2k [20]. The code was developed by P Blaha, allowing inclusion of local orbitals in the APW basis. Thus it improves upon linearization and makes possible a consistent treatment of semicore and valence in one energy window. The exchange and correlation effects are treated with the generalized gradient approximation (GGA) according to Perdew–Burke–Ernzerh [21].

In our case, the self-consistent field calculations are based on the following parameters: the atomic sphere radii (R_i) of 2.7, 2.0, 1.2, 2.0, 1.0, 0.7, 2.5, and 2.0 a.u. were used for

Table 1. Total energy E (Ryd) and magnetic moment M (μ_B) per unit cell are given for $\text{Fe}(\text{tz})_2\text{Cl}_2$, $\text{Cu}(\text{tz})_2\text{Cl}_2$ and $\text{Cu}(\text{tz})_2\text{Br}_2$. FM, AFM, and NM correspond to ferromagnetic, antiferromagnetic, and non-magnetic states, respectively.

	FM	AFM	NM
$\text{Fe}(\text{tz})_2\text{Cl}_2$			
E (Ryd)	-13 335.822	-13 335.968	-13 335.676
M (μ_B)	8.000	0.000	—
$\text{Cu}(\text{tz})_2\text{Cl}_2$			
E (Ryd)	-14 865.808	-14 865.869	-14 865.776
M (μ_B)	2.000	0.000	—
$\text{Cu}(\text{tz})_2\text{Br}_2$			
E (Ryd)	-32 031.362	-32 031.375	-32 031.338
M (μ_B)	1.998	0.000	—

Fe, Cl, N, S, C, H, Cu, and Br respectively. There are two magnetic metal (II) ions per unit cell for each compound. We chose the spin-polarized calculation for our calculation. We set the charge density Fourier expansion up to $l = 10$ and the charge density Fourier expansion cut-off $G_{\text{max}} = 10$ in the muffin-tins; 100 k -points in the first Brillouin zone were adopted in the calculations. In order to achieve a satisfactory degree of convergence, we specify charge and energy to be used as the convergence criterion, selecting charge and energy convergence to 10^{-4} .

3. Results and discussion

In the present paper, we performed the total energy calculations corresponding to ferromagnetic (FM), antiferromagnetic (AFM) and non-magnetic (NM) phases for $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($M = \text{Cu}, \text{Fe}$). Table 1 presents the total energy and magnetic moments of these three magnetic states. We found the AFM structure to be the lowest in energy, which indicates that the AFM phase is a stable ground state for $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($M = \text{Cu}, \text{Fe}$). In the non-magnetic phase the spin magnetic moment of each molecule is equal to zero, but for the AFM phase the spin magnetic moment of each molecule is not equal to zero: the spin arrangement of the neighbouring molecule is antiparallel, so the spin of the whole system is equal to zero. We choose a supercell. All atomic positions in the supercell are relaxed. In the FM calculations for $\text{Fe}(\text{thiazole})_2\text{Cl}_2$, we let the two Fe, Cl1, Cl2, S1, S2, N1, and N2 atoms of the supercell have the same spin magnetic moment orientation. In the AFM state for $\text{Fe}(\text{thiazole})_2\text{Cl}_2$, the spin arrangement is opposite, so in the AFM calculations we suppose that the two Fe, Cl1, Cl2, S1, S2, N1, and N2 atoms of the supercell have opposite spin magnetic moment respectively, and the other atoms are non-magnetic. That is to say, when we perform the AFM calculation, first we construct a unit cell which allows the desired AFM ordering, then flip the spin of one the AFM atoms (i.e. invert the spin up and down occupations), as a result we get the opposite spin magnetic moment corresponding to the atoms the spin of which is not flipped. In the NM calculations, we do not include the spin polarization. In the NM, FM, and AFM calculations, the same rule is used for $\text{Cu}(\text{thiazole})_2\text{X}_2$ ($X = \text{Br}, \text{Cl}$). From table 1 we can find that the FM state is a metastable state. In the NM calculations, the spin polarization is not included, thus no corresponding magnetic moments are shown.

The calculated total density of states (DOS) of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($M = \text{Cu}, \text{Fe}$) in the FM and AFM are given in figure 2. Figure 3 shows the partial DOS

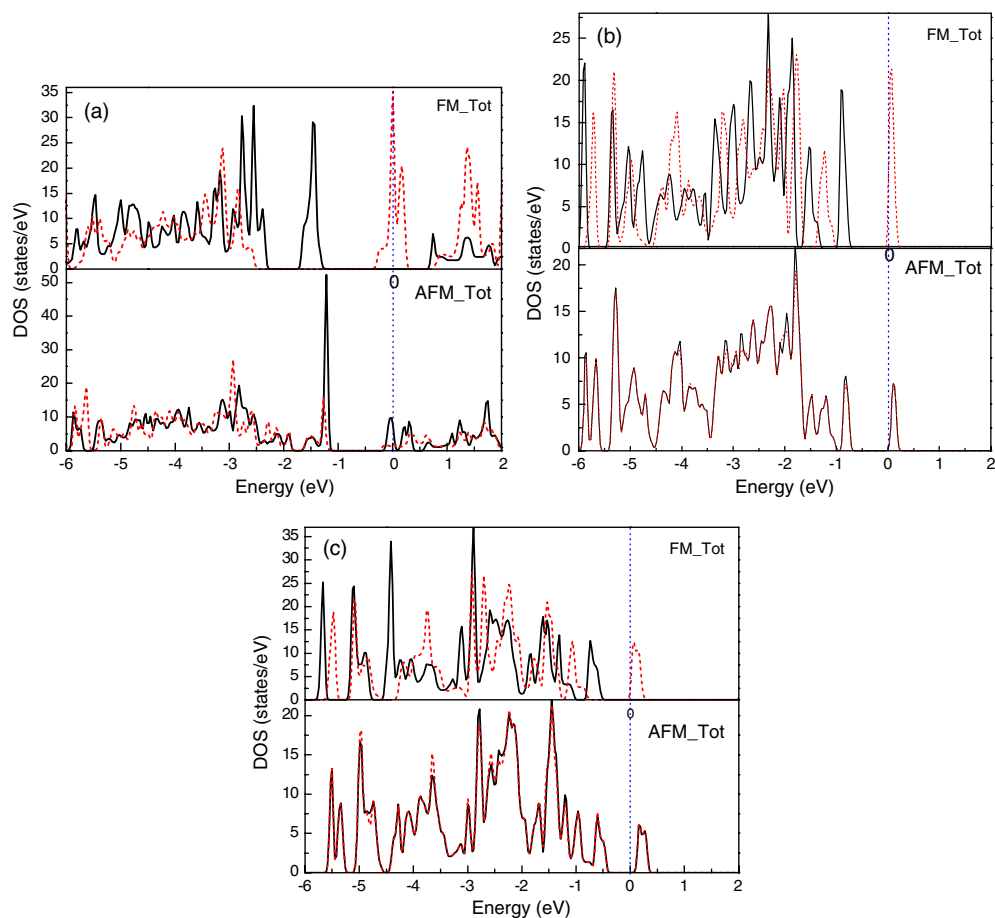


Figure 2. The calculated total density of states (DOS) for the molecule: (a) for $\text{Fe}(\text{tz})_2\text{Cl}_2$, (b) for $\text{Cu}(\text{tz})_2\text{Cl}_2$, and (c) for $\text{Cu}(\text{tz})_2\text{Br}_2$.

(PDOS) in the FM and AFM for $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$), where Fe' , Cl' and Br' are the atoms of the other molecules in the supercell for the AFM state. The plotted energy range is from -6 to 2 eV, and lower lying semi-core states have been omitted for clarity. Because the DOS distribution near the Fermi level determines the magnetic properties, we concentrate our attention on the DOS in the vicinity of the Fermi level, and the Fermi level is set to zero. In the vicinity of the Fermi level, the total DOS and the partial DOS are clearly split, which means that the ordered spin arrangement is formed by the exchange interaction. One valence band is split into two subbands: one is the spin-up valence band and the other is the spin-down valence band. In order to study the origin of the magnetic moment, we have studied the electronic structure of the compounds. From figure 2(a) it can be found that the total DOS for $\text{Fe}(\text{thiazole})_2\text{Cl}_2$ of the FM metastable state of the spin-up band has an energy gap, but that of the spin-down band is crossing the Fermi level, so the FM metastable state has half-metallic character. The spin-up and the spin-down DOS for $\text{Fe}(\text{thiazole})_2\text{Cl}_2$ of the AFM ground state in the Fermi level are all continuous, therefore the AFM state is metallic. From figures 2(b) and (c) we can find that the spin-up and spin-down total DOS in the ferromagnetic and antiferromagnetic phases of the compounds $\text{Cu}(\text{thiazole})_2\text{Cl}_2$ and

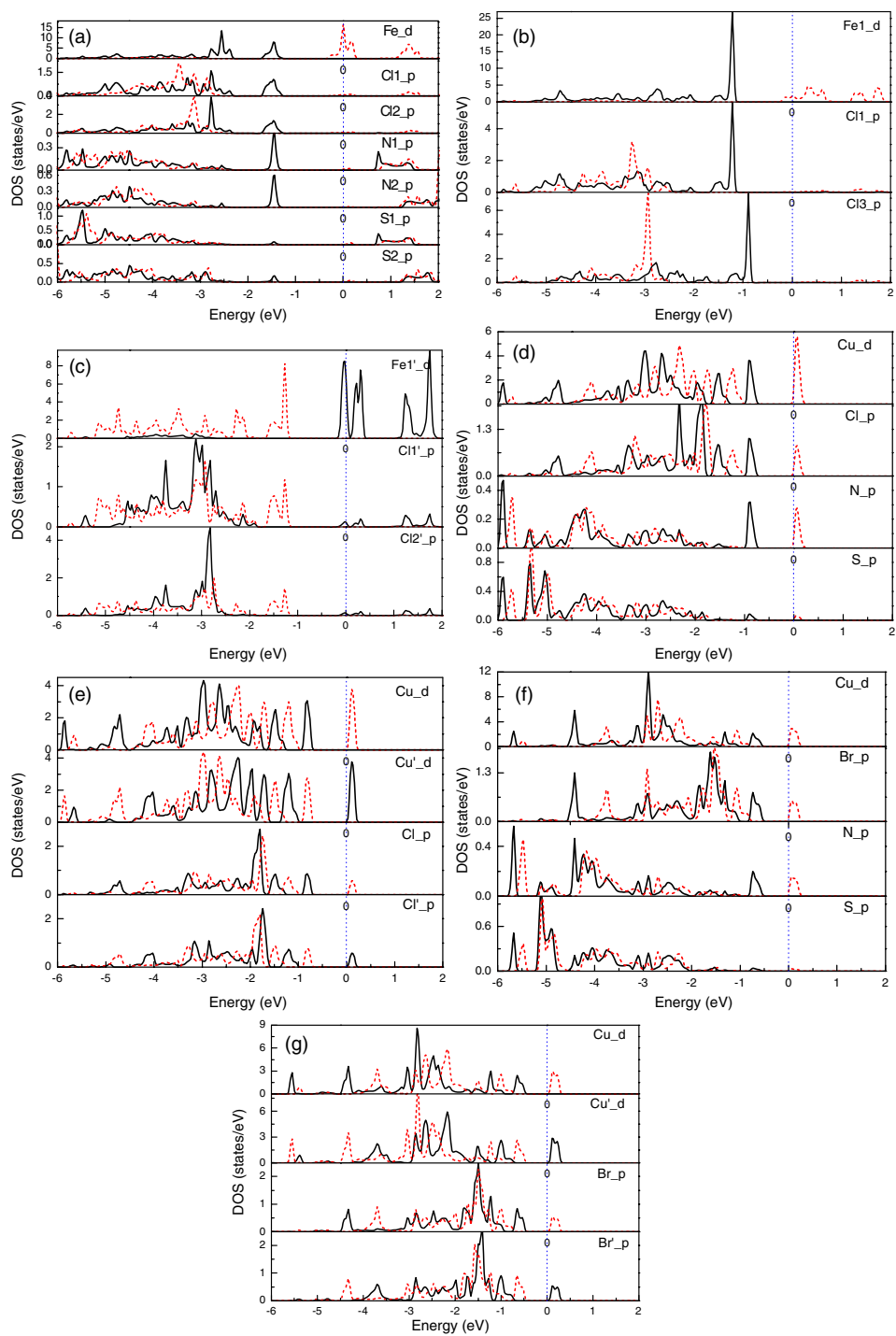


Figure 3. The calculated partial density of states (DOS) for $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$). The solid and dotted line denote majority and minority spin, respectively. The Fermi levels are located at 0 eV. (a) FM $\text{Fe}(\text{thiazole})_2\text{Cl}_2$; (b), (c) AFM $\text{Fe}(\text{thiazole})_2\text{Cl}_2$; (d) FM $\text{Cu}(\text{thiazole})_2\text{Cl}_2$; (e) AFM $\text{Cu}(\text{thiazole})_2\text{Cl}_2$; (f) FM $\text{Cu}(\text{thiazole})_2\text{Br}_2$; (g) AFM $\text{Cu}(\text{thiazole})_2\text{Br}_2$.

Table 2. Calculated magnetic moments in μ_B for the atoms of (a) $\text{Fe}(\text{tz})_2\text{Cl}_2$, (b) $\text{Cu}(\text{tz})_2\text{Cl}_2$, and (c) $\text{Cu}(\text{tz})_2\text{Br}_2$.

Atoms	Magnetic moment (μ_B)		Atoms	Magnetic moment (μ_B)
	FM	AFM		AFM
(a)				
Fe1	3.608	3.601	Fe1'	-3.601
Cl1	0.093	0.094	Cl1'	-0.094
Cl2	0.103	0.103	Cl2'	-0.103
S1	0.003	0.002	S1'	-0.002
S2	0.007	0.006	S2'	-0.006
N1	0.022	0.020	N1'	-0.020
N2	0.026	0.022	N2'	-0.022
(b)				
Cu	0.5503	0.5284	Cu'	-0.5284
Cl	0.0921	0.0935	Cl'	-0.0935
S	0.0070	0.0067	S'	-0.0067
N	0.0450	0.0457	N'	-0.0457
(c)				
Cu	0.4868	0.4653	Cu'	-0.4654
Br	0.1021	0.1105	Br'	-0.1104
S	0.0056	0.0052	S'	-0.0052
N	0.0463	0.0237	N'	-0.0237

$\text{Cu}(\text{thiazole})_2\text{Br}_2$ all opened a large bandgap. According to the DOS distribution in figure 3, we note that the main origin of magnetism is provided by the metal(II) 3d orbital; however, the Cl, Br, N, and S p orbitals also contribute to the spin magnetic moment, and the net spin of metal(II) 3d is parallel to that of Cl, Br, N, and S p. In addition, figure 3 shows that the partial DOS of the p orbitals of Cl, S, and N and the d orbital of iron in the compound $\text{Fe}(\text{thiazole})_2\text{Cl}_2$, and the partial DOS of p orbitals of Cl(Br), S, and N and the d orbital of copper in the compound $\text{Cu}(\text{thiazole})_2\text{Cl}_2$, $\text{Cu}(\text{thiazole})_2\text{Br}_2$ have similar peaks and character, and they occupy the same energy range, which means the electrons of these orbital have the same band structure or electronic structure and means these orbitals are mixed, so the p orbital of Cl, Br, S, and N and the d orbital of iron and copper are hybridized. In this way, the unpaired electron is formed and localized in the molecular orbital, which leads to the magnetism of the compounds.

For further consideration, we give the spin moments on atoms in table 2 of the AFM and FM states for $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$), where the spin moments are defined as the difference between the average numbers of occupied ions with the spin up and spin down in the muffin-tin sphere. From table 2, we find that the major part of the spin magnetic moment is from Fe(II) and Cu(II), indicating that the $\text{Fe}^{2+}(3d^6)$ configuration lies in the high-spin state and $\text{Cu}^{2+}(3d^9)$ configuration ions have one unpaired spin, which is in good agreement with the experimental result [13, 14]. There are also smaller positive spin populations on the chlorine, bromine, nitrogen, sulfur, and carbon atoms, which can be explained by the spin delocalization mechanism. The structures of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$) consist of tetragonally elongated octahedral units, with N-donor thiazole ligands in the axial positions. These units are equatorially linked along the

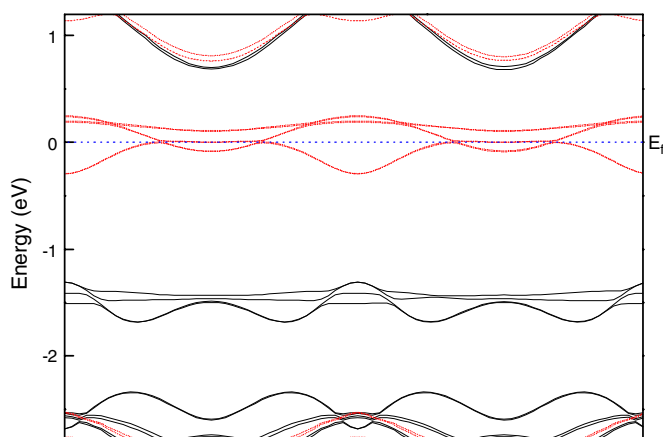


Figure 4. Electronic bands of FM state of $\text{Fe}(\text{tz})_2\text{Cl}_2$ along selected symmetry lines within the first Brillouin zone (the solid line is the up-spin electronic band; the dashed line is the down-spin electronic band).

b-axis by double dihalide bridges to form infinite linear chains, so the electronic states are delocalized. In these compounds, the Fe^{2+} ion with $3d^6$ in the high-spin state has four unpaired electrons and Cu^{2+} ions with $3d^9$ have one unpaired electron, which is why the spin magnetic moment of these compounds mainly comes from Fe^{2+} and Cu^{2+} , and partly from the chlorine, bromine, nitrogen, sulfur, and carbon atoms.

In order to further investigate the magnetic interaction and the conducting properties of compound $\text{Fe}(\text{thiazole})_2\text{Cl}_2$, we also give the electronic band structure of FM metastable state in figure 4. For clarity, we only plot the band structure in the range where there exists the spin-down highest occupied molecule orbital (HOMO) and the spin-down lowest unoccupied molecule orbital (LUMO) to discuss the conducting magnet character in the following. In figure 4 we show that the spin-down valence bands cross the Fermi level, and that there is no gap; however, there is an energy gap of 1.98 eV between the spin-down HOMO and spin-down LUMO, which implies that the FM metastate has half-metallic properties, which has potential for spintronic applications.

4. Conclusions

In conclusion, we have investigated the magnetic properties of $\text{Cu}(\text{thiazole})_2\text{Br}_2$ and $\text{M}(\text{thiazole})_2\text{Cl}_2$ ($\text{M} = \text{Cu}, \text{Fe}$) by employing DFT and GGA from the electronic band structure point of view. The results show that the Fe(II) complex is a metallic antiferromagnet and has a half-metallic ferromagnetic metastable state. But the spin-up and spin-down DOS in the ferromagnetic and antiferromagnetic phases of the compounds $\text{Cu}(\text{thiazole})_2\text{Cl}_2$ and $\text{Cu}(\text{thiazole})_2\text{Br}_2$ all open a large bandgap. The spin magnetic moment mainly comes from the Fe(II) and Cu(II) ions with some small contributions from the chlorine, bromine, nitrogen, sulfur, and carbon atoms.

Acknowledgment

This work was supported by the National Natural Science Foundation of China under grant Nos 10174023 and 20490210.

References

- [1] Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnar S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1488
- Osborne I S 2001 *Science* **294** 1483
- Awschalom D D and Kikkawa J M 1999 *Phys. Today* **52** (6) 33
- [2] Pickett W E and Moodera J S 2001 *Phys. Today* **54** (5) 39
- [3] de Groot R A, Mueller F M, van Engen P G and Buschow K H J 1983 *Phys. Rev. Lett.* **50** 2024
- [4] Coey J M D, Viret M and von Molnar S 1999 *Adv. Phys.* **48** 169
- [5] Soeya S, Hayakawa J, Takahashi H, Yamamoto C, Kida A, Asano H and Matsui M 2002 *Appl. Phys. Lett.* **80** 823
- [6] Watts S M, Wirth S, von Molnar S, Barry A and Coey J M D 2000 *Phys. Rev. B* **61** 9621
- [7] Matsumoto Y, Murakami M, Shono T, Hasagawa T, Fukawara T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 *Science* **291** 854
- [8] Ohno H 1998 *Science* **281** 951
- [9] Continenza A, Picozzi S, Geng W T and Freeman A J 2001 *Phys. Rev. B* **64** 085204
- [10] Xie W H, Liu B G and Pettifor D G 2003 *Phys. Rev. B* **68** 134407
- [11] Luo S J and Yao K L 2003 *Phys. Rev. B* **67** 214429
- [12] Yao K L, Zhu L and Liu Z L 2004 *Eur. Phys. J. B* **39** 283–6
- [13] Estes W E, Gavel D P, Hatfield W E and Hodgson D J 1978 *Inorg. Chem.* **17** 1415
- [14] James M, Kawaguchi H and Tatsumi K 1998 *Polyhedron* **17** 1843–50
- [15] James M 2000 *J. Phys. Chem. Solids* **61** 1865–70
- [16] Bonner J C and Fisher M E 1964 *Phys. Rev. A* **135** A640
- [17] Ziegler T 1991 *Chem. Rev.* **91** 651
- [18] Sosa C, Andzelm J, Elkin B C, Wimmer E, Dobbs K D and Dixon D A 1992 *J. Phys. Chem.* **96** 6630
- [19] Andzelm J and Wimmer E J 1992 *J. Chem. Phys.* **96** 1280
- [20] Blaha P, Schwarz K and Luitz J 1999 *WIEN97, A Full Potential Linearized Augmented Plane Wave Package for Calculation Crystal Properties, Karlheinz Schwarz (Techn. Universit Wien, Austria, 1999)* ISBN 3-9501031-0-4
- [21] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865