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Guest-Tuned Spin Crossover in Metal–Organic Frameworks

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This work is devoted to the analysis of the impact of halogen impurities on magnetic properties of the metal–organic framework Fe-MOF-74. Antiferromagnetic and ferromagnetic states have been studied in the guest-free Fe-MOF-74. We have found that this material is ferromagnetic at low temperatures below 4 K. The halogen absorption leads to the decrease of the intrachain exchange interaction between iron atoms and the increase of the interchain exchange. As a results, we observe the increase of the Curie temperature up to 89 K in the Br_2 absorbed Fe-MOF-74.

topics: metal–organic frameworks, halogens, guest-dependent magnetism, microporous magnet

1. Introduction

M-MOF-74 (M_2-DOBDC) is a group of porous coordination polymers made of divalent metals and 2,5-dihydroxy-benzene-1,4-dicarboxylate. The structure of the metal–organic frameworks (MOF) is characterized by infinite metal oxygen (M–O) chains in hexagons' vertices. These columns are connected by organic linkers creating 1D pores with a radius around 1.2 nm.

Transition-metal containing polymers are extensively investigated as lightweight magnets, magnetic separators, and magnetic sensors [1–5]. MOF-74 can be considered as a 1D magnet. Previous studies revealed strong intrachain exchange interaction, while the interchain exchange is significantly weaker [6, 7]. The existence of intrachain ferromagnetism with antiparallel chains magnetization has been verified.

Earlier, hydrocarbon-induced magnetism transition from ferromagnetic (FM) to antiferromagnetic (AFM) phase in Fe-MOF-74 have has obtained experimentally as well as theoretically [8, 9].

Herein, we report the results of *ab initio* study of halogen-induced ferromagnetism in the material Fe-MOF-74.

2. Methods

We have performed the ground state calculation within GGA-PBE [10], implemented in ABINIT code [11], using the projector augmented wave (PAW) basis [12]. Then Wannier functions and Hamiltonian have been extracted in order to evaluate exchange parameters, using Green's function approach implemented in the TB2J code [13]. The temperature dependence of the magnetic moment and susceptibility have been obtained using the MULTIBINIT code implemented in the ABINIT package. The elementary cell contains 54 atoms and belongs to the space group R-3 [148]; the Bravais lattice is rhombohedral (hR).

The crystal structure of the guest free Fe-MOF-74 has been optimized by using Broyden–Fletcher–Goldfarb–Shanno minimization.

It has been reported previously that halogens in MOFs with open metal sites are in two phases [14]. At low temperatures and low pressure, halogens are in an oxidized phase (Fig. 1a). The increase of temperature leads to cleavage of the transition metal–halogen bonds, molecules formation (Fig. 1b) and concomitant release of halogens. Taking this into account, we performed *ab initio* calculations for two halogens phases, i.e., oxidized and molecular. We assumed that absorbed molecular and atomic halogens do not affect Fe-MOF-74 significantly. Thus, we fixed the atomic positions and unit cell parameters of Fe-MOF-74 during halogen's coordinates optimizations.

Both FM and AFM states have been considered in guest-free Fe-MOF-74. The AFM configuration is described by antiparallel alignment of neighbour chains, and the corresponding space group is rhombohedral R-3 [148] with magnetic group -3' containing six elements.

3. Results and discussion

Ground state calculation in the guest free Fe-MOF-74 resulted in the same value of iron magnetization, i.e., 2.0 μ_B. We can observe the strong exchange interaction along the Fe–O chain. The value of the exchange integral J_{intra} is 8.2 meV in the case

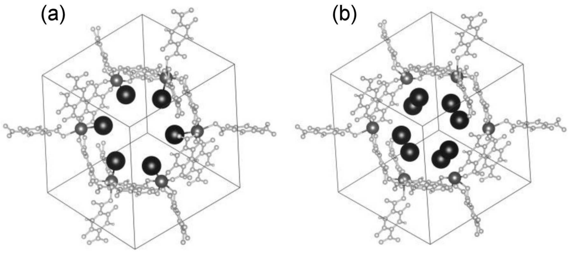

Fig. 1. The optimized periodic structure of the Fe-MOF-74 with Br (a) and Br_2 (b) impurities. The largest black spheres — bromine, dark grey — iron, light grey — organic linkers. In the case of chlorine, the elementary cell also contains 6 chlorine atoms or 4 molecules of Cl_2.

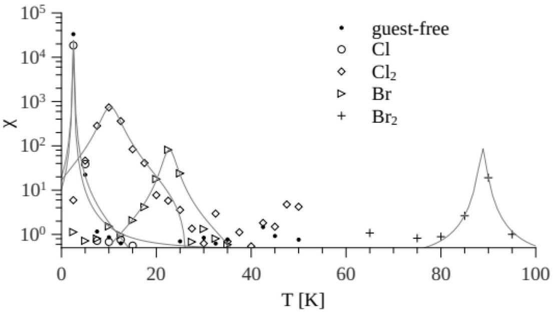

Fig. 2. Relative magnetic susceptibility in the Fe-MOF-74. Scatter plots correspond to the Multibinit's results; lines show their Lorentzian fit.

of AFM phase (Table I). In Fe-MOF-74, the value of $J_{\rm intra}$ is even higher and equals 10.2 meV. The distance between iron atoms inside a chain is 2.95 Å, whereas the distance between the closest iron atoms of neighbour chains is 7.61 Å. The value of $J_{\rm inter}$ is around one order of magnitude less than $J_{\rm intra}$ in AFM Fe-MOF-74. In the case of FM state, the value of $J_{\rm inter}$ is even smaller. Statistical calculations of dynamical magnetic properties resulted in the Curie temperature around 3 K (Fig. 2). The experimental study shows high values of $J_{\rm intra}$ at temperatures below 10 K, proving superparamagnetism in the Fe-MOF-74 [7].

In the case of chlorine oxidized Fe-MOF-74, the $J_{\rm intra}$ is lower than in the guest-free material, while the $J_{\rm inter}$ is still low. Thus the Curie temperature $T_{\rm C}$ is not increased (Table II). Here the average Fe–Cl distance is 2.86 Å, and the average value of $J_{\rm Fe-Cl}$ is 0.3 meV, whereas $J_{\rm Cl-Cl}$ is less than 0.01 meV.

With molecular chlorine, the value of $J_{\rm intra}$ is the same and equals 6.2 meV, but the value of $J_{\rm inter}$ improves up to 0.2 meV. Thus the Curie temperature $T_{\rm C}$ is higher and equals 10 K.

In Fe-MOF-74 oxidized by bromine, we observe the lowest value of $J_{\rm intra}$, which equals 1.9 meV. Here the average Fe–Br distance equals 2.8 Å, and the average $J_{\rm Fe-Br}$ is 3.1 meV. The value of the exchange integral between bromine atoms is around 0.1 meV.

TABLE I

Magnetic properties of the guest-free Fe-MOF-74. The average magnetization of a Fe atom is M_{Fe}; $J_{\rm intra}$ and $J_{\rm inter}$ correspond to the exchange energy between nearest Fe atoms inside a chain (intra) and between nearest Fe atoms of neighbour chains (inter), $T_{\rm N}$ stands for the Neel Temperature.

	$M_{\rm Fe}[\mu_B]$	$J_{\rm intra}$ [eV]	$J_{\rm inter}$ [eV]	$T_{\rm C}$ ($T_{\rm N}$) [K]
AFM	2.0	8.7	-0.7	< 1
FM	2.0	10.2	< 0.1	3

TABLE II

Magnetic properties of the ferromagnetic Fe-MOF-74 with halogen impurities. The average magnetization of a Fe atom is M_{Fe}; $J_{\rm intra}$ and $J_{\rm inter}$ correspond to the exchange energy between nearest Fe atoms inside a chain (intra) and between nearest Fe atoms of neighbour chains (inter).

	$M_{\rm Fe}[\mu_B]$	$J_{\rm intra}$ [eV]	$J_{\rm inter}$ [eV]	$T_{\rm C}$ [K]
Cl	2.6	6.2	< 0.1	3
Cl_2	2.0	6.2	0.2	10
Br	2.5	1.9	0.2	23
Br_2	2.1	10.2	0.3	89

In the case of molecular bromine, we observe the highest value of $J_{\rm inter}$, while the value of $J_{\rm intra}$ is also high and close to the one obtained in the guest-free Fe-MOF-74.

4. Conclusions

Ground state properties of the ferromagnetic phase in the guest-free and halogen absorbed material Fe-MOF-74 have been obtained within the GGA approach. Then we calculated the exchange parameters using the Wannier functions and Green's function approach. The Fe-MOF-74 is characterized by the strong exchange interaction inside the Fe–O chain, while the interchain exchange is weak. In this material, the ferromagnetic is observed at low temperatures below 4 K. We have found that halogens lead to a decrease in intrachain exchange as well as to an increase in interchain exchange. Thus we observe higher Curie temperature in the halogen containing material than in the guest-free one. The highest values of the interchain exchange and the Curie temperature have been defined in the molecular bromine absorbed material Fe-MOF-74, and are 0.3 meV and 89 K, respectively.

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