Long-range Ferromagnetic Ordering and Magnetic Phase Transition in Metal-organic Frameworks

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Abstract

A magnetic phase transition is observed in a metal-organic framework (MOF-505) using SQUIDs. The MOF-505 shows weak ferromagnetism with a Curie Temperature of 11 K and antiferromagnetism at high temperature. Meanwhile, a spin-Peierls-like phase transition occurs at 164 K. The magnetic phase transition and the gap-like magnetic behavior derive from defects. The strong localized states of defects induce spontaneous spin polarization and local magnetic moments. Electronic structure calculations based on density functional theory illustrate that π electrons in the aromatic linkers mediate these defect-induced local moments to form long-range Stoner ferromagnetism.

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Metal-organic frameworks (MOFs) are three-dimensional (3D) porous network structures consisting of inorganic metal-oxide clusters linked by one-dimensional (1D) organic chains. This new class of materials show a number of promising applications such as hydrogen storage, methane storage, molecular sieves and catalysis. Due to the constitutive open-shell transition metal (TM) ions, some of the MOFs exhibit unique magnetic property which is attracting much attention because of their potential applications in low density magnetic materials, molecular magnets, and magnetic sensors. Very recently, Sun et al. proposed that hydrogen storage ability of MOF could be affected by the spin state of magnetic metallic ions.

The building block of magnetic MOFs is a dimeric copper carboxylate cluster which has a paddle-wheel-like structure. Its magnetism is derived from the unpaired electrons in the $d^9$ shell of the two copper ions. Strong superexchange antiferromagnetic (AFM) coupling was reported for the magnetic interaction between the two copper ions, i.e., the two copper ions in the dimeric copper carboxylate cluster have opposite spins which results in zero total magnetic moment at low temperature. However, ferromagnetism (FM) was observed in a number of recently discovered MOFs with antiferromagnetic dimeric copper acetate components linked by nonmagnetic organic chains at low temperature, and the HKUST1 is a typical example. Consequently, questions such as the following arise. What is the origin of the local magnetic moments in these structures and how do these local magnetic moments couple each other to produce a collective magnetism? To date, there have been no satisfactory answers to such questions and the mechanism of ferromagnetism in the MOFs remains unclear. Model based on a strong AFM interaction between the Cu atoms in the cluster and a weak FM inter-cluster interaction was proposed. However, given the strong AFM coupling between the Cu ions within a cluster and the large separation between the clusters (9.5 – 14.4 Å in MOF-505), whether the AFM cluster can generate a sufficiently large local moment is in question, and even if it does, how these local moments are coupled over a large distance is not trivial. Meanwhile, it is known that local magnetic moments can be produced by defects in various crystals. Since the AFM coupled Cu dimer in the dimeric copper carboxylate cluster is unlikely to produce any local magnetic moment, and simple defects such as vacancies are the most common defects in crystal growth, it is natural to examine models based on such simple defects.

One way to determine whether defects play a role in the magnetic properties of a 1D...
or quasi-1D material is the spin-Peierls (SP) transition. This magneto-elastic transition is known to occur in antiferromagnetically coupled $S = 1/2$ Heisenberg model. Below the SP transition temperature ($T_{SP}$), an energy gap occurs in the spectrum of magnetic excitation, which is due to magnetic impurities or defects in the crystal. The SP or SP-like transition has been found in several organic or inorganic compounds, but so far it has not been reported in inorganic-organic hybrid materials.

In this Letter, we report results of our investigation on the magnetic properties of single crystal MOF-505. We observed, for the first time in an inorganic-organic system, a SP-like transition at $T_{SP} = 164$ K. Furthermore, MOF-505 was found to be ferromagnetic below 11 K. Theoretical study based on density functional theory (DFT) calculations revealed that local magnetic moments originate from copper vacancies in the dimeric copper carboxylate clusters, and the long-range ferromagnetic coupling between these local moments is mediated by the delocalized $\pi$ electrons in the aromatic linkers. It is known that $\pi$ electrons in aromatic organic materials are able to mediate defect-induced local magnetic moments over a considerable distance to form the so-called “Stoner” magnetism. For example, the coupling distance of local moments induced by carbon vacancies can be up to 20 Å in graphene which can be considered as a conjugated network of aromatic rings. We emphasize that this mechanism is different from the traditional understanding of long-range interaction in defect-induced intrinsic ferromagnetism in solid-state materials, such as nitrides and oxides, where overlap of extended wave functions of the defects are essential for magnetic interaction.

Single crystal MOF-505 was synthesized using the same method as reported elsewhere. The MOF is a 3D network structure composed of the paddle-wheel-like inorganic Cu$_2$(CO$_2$)$_4$ cluster nodes linked by the 1D organic bptc$^{4-}$ units, as shown in Fig. 1. The magnetic properties are measured using a superconductor quantum interference device (SQUID). The samples were sealed in a straw (provided by Quantum Design Inc.) with a very weak magnetic signal ($< 10^{-6}$ emu), so that the magnetic signal of the samples can be accurately measured. The susceptibility was measured by applying a magnetic field of 5 KOe and the temperature range was 2 to 300 K. The magnetic properties of copper (II) dinuclear carboxylate molecules [see Fig. 1(a)] were measured first. The measured susceptibility of the copper(II) dinuclear molecule is shown as a function of temperature in Fig. 2(a). It is obvious that the molecule is antiferromagnetic which is in good agreement with findings of
other experiments. As a matter of fact, the organic molecular chain is a biphenyl group [Fig. 1(b)] and is a typical nonmagnetic material. However, when these two compounds are synthesized into a single crystal MOF-505, it shows a completely different magnetic property. Figure 2(b) shows the dependence of susceptibility of MOF-505 with OH$_2$ ligands (circles) and dehydrated MOF-505 (diamonds), respectively, on temperature. Both curves show typical spin-singlet features at high temperature, similar to that of the antiferromagnetic copper (II) dinuclear molecules. At low temperature, however, the material shows an unexpected weak ferromagnetic property. Furthermore, we found that this magnetic phase transition in MOF-505 is not affected by the applied magnetic field. For example, there is only a slight difference between the zero field cooled (ZFC) and field cooled (FC) susceptibilities. We also varied the field strength from 100 Oe to 50 KOe and found no noticeable changes in the $\chi$-$T$ curve. We fitted the susceptibility data of MOF-505 with OH$_2$ ligands at low temperature to the Curie-Weiss law,

$$\frac{1}{\chi} = \frac{1}{C}(T - T_c)$$

where $\chi$ is the magnetic susceptibility, $C$ is the Curie constant, and $T_c$ is the Curie temperature, and obtained a $T_c$ of 11 K, as shown in the insert of Fig. 2(b). This value is higher than that of HKUST-1 (4.7 K). The positive Curie temperature indicates a weak-ferromagnetism at low temperature, which can also be proved by the magnetic hysteresis loop at 5 K shown in Fig. 2(c). Furthermore, a gap-like feature occurs near 164 K, below which the susceptibility decreases abruptly with decreasing temperature, indicating a phase transition. It is well known that all materials exhibiting SP transition have the same characteristic $\chi - T$ phase diagram, which was first proposed by Cross and Fischer. For example, several different inorganic and organic SP compounds have a striking similarity: their susceptibility curve suddenly decreases with reducing temperature at the SP transition temperature $T_{SP}$. Since the SP transition can be due to either magnetic impurities or defects, we next investigate the possible reason for the SP transition in MOF-505. Since the materials were synthesized in solutions, no magnetic impurities were introduced in our experiment except for the nonmagnetic OH$_2$ ligands. To find out the effect of water impurities on the magnetic property of MOF-505, we annealed the samples at 400 K for 2 h. The temperature dependence of the susceptibility of the annealed sample is similar to that of MOF with OH$_2$ ligands [see Fig. 2(b)], except that the two curves separate near $T_{SP}$. This means that the
SP-like transition in MOF-505 was affected by the dehydration. We believe that besides water is removed from the interior of the MOF, the annealing process also removes OH ligands attached to the Cu atoms, which is supported by experiments. Removing the ligands will affect the Cu-Cu distance, and the structural distortion could affect the SP transition.

To delineate the formation of local moments and investigate the roles of long-range magnetic interaction in MOF-505, we carried out DFT calculations. We consider first a single copper vacancy ($V_{Cu}$) which is modeled by removing a copper atom in the unit cell of MOF-505. The formation entropy of the copper vacancy in MOF-505, defined as $E_f = E_{\text{defect}} + E_{Cu} - E_{\text{pure}}$, where $E_{\text{pure}}$ and $E_{\text{defect}}$ are the total energies of MOF-505 before and after the Cu atom is removed to create the Cu vacancy, respectively, and $E_{Cu}$ is the energy of an isolated copper atom, was found to be 2.5 eV. Moreover, $V_{Cu}$ favors a spin-polarized state and the polarization energy (energy difference between the spin-polarized state and non-spin-polarized state) is 199 meV. Each Cu vacancy introduces a magnetic moment of 0.73 $\mu_B$ in MOF-505. To show the spin density clearly, we first show in Figs. 3(a) and 3(b) the expanded views of the shaded areas in Figs. 1(d) and 1(e), respectively. Figure 3(c) then displays an isosurface of spin density of MOF-505 with one copper vacancy. It is clear that the defect states are mainly localized on the neighboring O and C atoms, and therefore are of characteristic of $p$-orbitals. This localized defect state leads to a spin-polarized ground state and results in a local magnetic moment of $\sim 0.73\mu_B$ per Cu vacancy. For comparison, we performed similar calculations on another MOF compound, MOF-11, which has the same Cu(II) building block as MOF-505, and obtained a vacancy formation entropy of 2.8 eV, a polarization energy of 32 meV, and a magnetic moment of 0.97 $\mu_B$ per Cu vacancy for MOF-11. This confirms that the local magnetic moments in MOFs are provided by copper vacancies in the Cu$_2$(CO$_2$)$_4$ cluster nodes.

With this understanding on the origin of local magnetic moments, we next investigate the long-range magnetic coupling between the local moments. It is generally believed that extended tails of defect wavefunctions are responsible for mediation of long-range exchange interaction between defect induced local moments, which is the mechanism of magnetic coupling in nitrides and oxides. However, there is a limit on the range of such interaction. Osorio-Guillen et al. argued that ferromagnetic interaction between two vacancies is effective up to four neighbors. For example, wavefunction of oxygen 2$p$ orbital
around a Ca vacancy in CaO extends no more than 5.5 Å. In the MOF being studied, the
defect states are mainly localized on neighboring anions around the copper vacancies, which
is similar to that of nitrides and oxides. However, the distance between the vacancies ranges
from 9.5 Å to 14.4 Å which is much longer than the above coupling range. We also studied
the spatial extensions of C 2p and Cu 3d orbitals and found that the C 2p orbitals have
similar localization as O 2p while the 3d orbitals of Cu is more localized than the above 2p
orbitals. This indicates that neither the 2p orbitals of C or O nor the 3d orbitals of Cu have
wavefunctions with sufficient spatial extension to mediate the long-rang magnetic coupling
in MOF and we must seek an alternative mechanism that can couple the defect induced
local magnetic moments ferromagnetically at low temperature. Recently, it was proposed
that delocalized π electrons in graphene are able to mediate magnetic coupling over a along
range in defect-induced “Stoner” magnetism, and the coupling distance, between
local moments induced by carbon vacancies, can reach 20 Å in graphene. In MOF-505,
the dimeric copper carboxylate clusters are linked by aromatic compounds which also have
π electrons as in graphene. It is not unreasonable to believe that ferromagnetic coupling
between local magnetic moments induced by Cu vacancies in MOF is mediated by these
delocalized π electrons in the aromatic linkers.

To verify this hypothesis, we introduced a pair of copper vacancies into the supercells
of both MOF-505 and MOF-11. As mentioned before, the two MOFs consist of the same
inorganic Cu2(CO2)4 cluster nodes but different linkers (Fig. 1). The linker in MOF-505
is an aromatic organic compound with delocalized π electrons, but that in MOF-11 is an
inorganic adamantane, without delocalized π electrons. The two copper vacancies, created
by removing the Cu atoms in two neighboring coper-oxide clusters, are separated by 14.4 Å
and 14.2 Å in MOF-505 and MOF-11, respectively. Results of our spin-polarized total energy
calculations show that the two local moments in MOF-505 favor FM coupling ($E_{FM} - E_{AFM} =
-23$ meV) with a resultant magnetic moment of 1.17 $\mu_B$. In contrast, the FM and AFM
states of MOF-11 have comparable energies. We also compared the spin-projected local
densities of states (LDOS) at the vacancies of the FM and the AFM states and found they
are identical except the different orientations of the local magnetic moments. This indicates
no coupling between the local magnetic moments in MOF-11. Figures 3(e) and 3(f) show
the spin densities of MOF-505 and MOF-11, respectively. It is clear that aromatic linker
mediates the magnetic coupling in MOF-505 but the inorganic adamantane linker does not
in MOF-11. In MOF-505, the FM order of defects competes with the AFM of Cu$_2$(CO$_2$)$_4$
cluster nodes. If the defect concentration is sufficiently high, MOF-505 will show weak
ferromagnetism. But the orientation of local moments in MOF-11 is disorder. Consequently,
MOF-11 is still in its singlet state at low temperature which is in agreement with earlier
experimental result.[17]

We wish to point out that the organic molecular linker in MOF-505 (Fig. 1(b)) is dif-
derent from a usual biphenyl group. Due to the constraint of the network structure, the
biphenyl group here is a rather rigid planar molecule, and thus a perfect conjugated system.
The carbon rings of a normal biphenyl molecule can be easily rotated around the σ bond
connecting the two rings, and therefore, the two phenyl groups are normally not co-planar
which does not favor formation of the large π bond. It is also noted that the biphenyl group
is different from the phenyl group which forms the main part of the linker in KHUST-1.
As we discussed above, HKUST-1 has a similar ferromagnetic properties as MOF-505, but
a lower Curie temperature, which could be related to the difference between phenyl and
biphenyl groups.

In conclusion, we observe a magnetic phase transition and a spin-Peierls-like transition
in MOF-505. The transition temperatures are $T_c = 11$ K and $T_{SP} = 164$ K, respectively.
Copper vacancies are responsible for the formation of local magnetic moments. Intrinsic
ferromagnetism in the MOF-505 is mediated by delocalized π electrons of the aromatic
organic linkers. This mechanism of ferromagnetic coupling over a considerably long-range is
fundamentally different from the conventional understanding of defect-induced magnetism
in 3D solid-state materials.

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We performed total-energy calculations using first-principles method. The VASP code was used with the generalized gradient approximation for the exchange correlation and projector augmented wave method. The energy cutoff was 400 eV. A $k$-mesh of $3\times3\times3$ was used in unitcell (96 atoms of MOF-505, 72 atoms of MOF-11) and only gamma point was used in supercell ($2\times2\times2$ unitcell). All atoms were allowed to relax until the Hellmann-Feynman forces acting on them become less than 0.02 eV/Å.
FIG. 1: (Color online) Schematic diagram showing assembly of MOF-505 (d) and MOF-11 (e) from a basic “paddle-wheel-like” building unit (a), a rigid organic linker with aromatic properties (b), and an adamantane cluster linker (c). Enlarged views of the shaded areas in (d) and (e) are given in Fig. 3(a) and Fig. 3(b), respectively.

FIG. 2: (Color online) (a) The temperature dependence of susceptibility ($\chi$) of the copper (II) dinuclear molecule which is the basic building block of MOF-505 and MOF-11. (b) The temperature dependence of susceptibility of MOF-505 with (diamonds) and without (circles) OH$_2$ ligand. Both (a) and (b) are measured under a magnetic-field of 5 KOe. The insert of (b) shows the $1/\chi - T$ curve in the temperature range 0 – 75 K. The solid line is the curve fitted to the Curie-Weiss law. (c) The magnetic hysteresis loop of MOF-505 at 5 K.

FIG. 3: (Color online) (a) and (b) are enlarged views of the shaded areas in Figs. 1(d) and 1(e). (c) and (d) show the spin densities of MOF-505 and MOF-11 with a single copper vacancy, respectively. (e) and (f) are the spin densities of MOF-505 and MOF-11 with a pair of copper vacancies, respectively. Note that the orientation of two local moments is disorder in MOF-11. The distance between the two vacancies are indicated. The isovalue are 0.03 e/Å$^3$ for (c) and (d) and 0.01 e/Å$^3$ for (e) and (f).
Fig. 1 Shen et al.
Fig. 2 Shen et al.
Fig. 3 Shen et al.