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Phys. Rev. B **87**, 094407 — Published 7 March 2013

DOI: [10.1103/PhysRevB.87.094407](https://doi.org/10.1103/PhysRevB.87.094407)

# When metal organic frameworks turn into linear magnets

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(Dated: February 11, 2013)

We investigate the existence of linear magnetism in the metal organic framework materials MOF-74-Fe, MOF-74-Co, and MOF-74-Ni, using first-principles density functional theory. MOF-74 displays regular quasi-linear chains of open-shell transition metal atoms, which are well separated. Our results show that within these chains—for all three materials—ferromagnetic coupling of significant strength occurs. In addition, the coupling in-between chains is at least one order of magnitude smaller, making these materials almost perfect 1D magnets at low temperature. The inter-chain coupling is found to be anti-ferromagnetic, in agreement with experiments. While some quasi-1D materials exist that exhibit linear magnetism—mostly complex oxides, polymers, and a few other rare materials—they are typically very difficult to synthesize. The significance of our finding is that MOF-74 is very easy to synthesize and it is likely the simplest realization of the 1D Ising model in nature. MOF-74 could thus be used in future experiments to study 1D magnetism at low temperature.

PACS numbers: 75.10.Pq, 75.25.-j, 75.75.-c, 75.40.Cx

The continued quest for the development of non-volatile memories and spintronic devices of smaller sizes requires the full comprehension of finite-size effects. To this end, over the last decade, exotic magnetic properties have received much attention in experimental and theoretical studies.<sup>1–14</sup> Considerable emphasis has been given to the synthesis and prediction of materials showing mono-dimensional magnetism,<sup>1–14</sup> also referred to as *1D* or *linear* magnetism. While 1D magnetism can be explained with the well-understood Ising model (dating back to 1925),<sup>15</sup> a satisfactory physical realization of this model in simple materials has not yet been found and 1D magnetism is only observed in a few—often difficult<sup>8,10,14</sup> or dangerous<sup>9</sup> to synthesize—synthetic inorganic materials and polymers. Although, for example, CrSb<sub>2</sub> is one of the few materials that shows naturally 1D anti-ferromagnetism, this property remains difficult to control and tune.<sup>14</sup> In fact, theory has shown that strong spin fluctuations induce ferromagnetic disorder of 1D-spin arrays at any temperature, independent of the extent of exchange interactions between neighboring spins.<sup>15,16</sup> Thus, progress in the field of 1D magnetism crucially depends on the availability of currently missing simple-to-synthesize model systems and materials.

The main difficulty in engineering good model systems exhibiting 1D magnetism are:<sup>2,10</sup> (i) to find materials that have quasi-1D chains of spins with significant interactions and large magnetic anisotropy, (ii) to find materials with a large ratio between intra and inter-chain magnetic interactions, (iii) to find materials in which ferromagnetism is preserved at “reasonable” low temperatures, (iv) to find materials with very few impurities, which tend to destroy ferromagnetism, and finally (v) to find materials that are simple, safe, inexpensive to synthesize, and where linear magnetism is easy to control. Historically, the engineering of 1D magnetic materials

has followed several routes. Attempts were made using inorganic materials such as Sr<sub>2</sub>Cu(PO<sub>4</sub>)<sub>2</sub>, Sr<sub>2</sub>CuO<sub>3</sub>,<sup>4</sup> and BaCo<sub>2</sub>V<sub>2</sub>O<sub>8</sub>,<sup>11</sup> along with non-periodic magnetic clusters or molecular magnets.<sup>10</sup> Another strategy is the combination of organic molecules and transition metals (TM) to form regular polymer 1D magnets.<sup>2,8,10,13</sup> The latter strategy offers a larger degree of freedom due to the high tunability of the diamagnetic organic separators, which can promote spin localization on the central TM.<sup>2,8,10</sup>

We propose here that metal organic frameworks (MOFs), a novel class of nano-porous materials, offer a versatile platform for the realization of 1D magnets due to their high tailorability and tunability that results from their discrete molecular building-block nature.<sup>17–20</sup> For this reason MOFs are already targeted in a large variety of applications such as gas-separation, gas-sensing, gas-capture, catalysis, and drug-delivery.<sup>17–22</sup> In particular, in the following, we argue that the structural simplicity, low cost, and ease of synthesis of MOF-74—together with the already existing understanding of this material—fulfill the criteria mentioned above and thus make it an outstanding candidate for studying linear magnetism. Note that signatures of 1D-ferromagnetism in MOF-74-Co were already observed experimentally by Dietzel *et al.* in their pioneering work on this MOF.<sup>23</sup> From Fig. 1 it is apparent that MOF-74-TM (with TM = Mn, Fe, Co, Ni, and Cu) can be seen as 1D magnet since it displays regular pseudo-chains of transition metals aligned along the basal plane. The helicoidal chains resulting from the atomic-motif of Fig. 1a are interspaced by “long” organic linkers, suggesting that the inter-chain interactions are quenched. In fact, MOF-74 shows a large structural ratio ( $\sim 3$ ) between the separation of spins in a chain compared to chain separation (see Fig. 1), establishing a required condition for the construction of a 1D magnet.

To elucidate the 1D-like magnetic properties exhib-

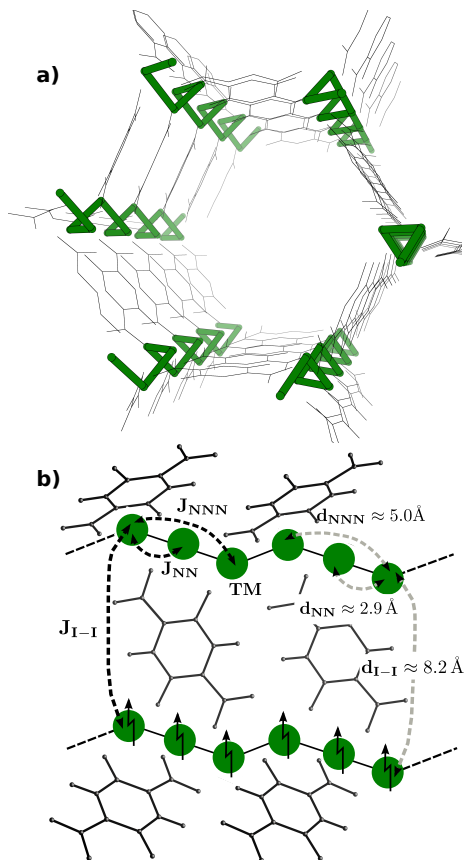


FIG. 1. **a)** Frontal view of MOF-74, helicoidal magnet chains are highlighted in green. **b)** side view of MOF-74, TM atoms are represented by green balls.  $d_{NN}$  and  $d_{NNN}$  are the nearest-neighbor and next-nearest-neighbor intra-chain distances, while  $d_{I-I}$  is the inter-chain distance. The couplings  $J_{NN}$ ,  $J_{NNN}$ , and  $J_{I-I}$ , are defined in parallel.

ited by MOF-74, we study the three isostructural materials MOF-74-Fe,<sup>24</sup> MOF-74-Co,<sup>23</sup> and MOF-74-Ni.<sup>25</sup> To this end, we use density functional theory (DFT) with the PBE functional, as implemented in QUANTUMESPRESSO.<sup>26</sup> We employ ultrasoft pseudopotentials with wave-function and density cutoffs of 680 eV and 6800 eV. The pseudopotentials used for the TM (i.e. Fe, Co, and Ni) are also suitable for spin-orbit calculations including relativistic corrections. The total energy is sampled with a  $2 \times 2 \times 2$   $k$ -point mesh, resulting in energy differences converged to within less than 1 meV. Projected density of states onto selected atomic orbitals are performed on a denser  $k$ -point mesh, i.e.  $4 \times 4 \times 4$ . The SCF total energy convergence criterium is  $1.4 \times 10^{-10}$  eV. We need such tight criteria to be able to accurately sample the delicate energy landscape originating from different spin arrangements.

All calculations are performed on the experimental structures of MOF-74-Fe,<sup>24</sup> MOF-74-Co,<sup>23</sup> and MOF-74-Ni,<sup>25</sup> which crystallize in a rhombohedral primitive cell with 54 atoms and space group  $R\bar{3}$ . The calculation of

TABLE I. MOF-74-TM net atomic charges (in units of the electronic charge),  $Q_O$  and  $Q_{TM}$ , and electron population of  $p$  and  $d$  orbitals on O and TM atoms,  $q_O(2p)$  and  $q_{TM}(3d)$ , respectively. Magnetic moments,  $\mu$ , are reported in units of  $\mu_B$ .

TM	$Q_O$	$q_O(2p)$	$Q_{TM}$	$q_{TM}(3d)$	$\mu$
Fe	-0.30	4.75	+0.50	6.35	3.625
Co	-0.95	5.35	+2.49	5.17	3.255
Ni	-0.61	4.94	+1.24	8.33	1.567

the intra-chain  $J$ -coupling constants requires the freedom to have varying spin directions along a chain. But, the primitive cell of MOF-74-TM contains only 6 TM atoms that all belong to different chains (1 per chain), which does not give the required freedom. Thus, we construct a supercell extending the unit cell along the chain direction, such that each unit cell now contains two chains with 6 TM atoms per chain, and a total of 108 atoms. Coordinates and relative lattice constants of the supercells are reported in the Supplementary Information.

Linear magnetism relies on ferro- or antiferromagnetism that can only exist if the TM atoms have a non-negligible magnetic moment. We therefore begin by analyzing the localization of the magnetic moment on the TM atoms, combining the projected density of states and the Löwdin population analysis. The Löwdin analysis, similarly to the Mulliken analysis is an intuitive (but not unique) way of re-partitioning the electron charge density on each atom (and orbital), by projecting it onto individual orthonormalized atomic orbitals.<sup>27</sup> Table I shows the Löwdin charges, relative contribution, and magnetic moments of the TM and O atoms in the three MOF-74 investigated. The magnetic moments,  $\mu$ , were computed by integrating the spin-densities difference ( $\rho_{up} - \rho_{down}$ ) of the  $d$ - $p$  orbitals in the valence region of each TM. Although it is inadequate to draw decisive conclusions from the charge analysis of Table I, we observe that oxygen atoms in MOF-74 assume an interesting covalent nature, having repercussions on the final charges and magnetic moment of the TM in MOFs. We further confirm the local charge of Co in MOF-74-Co (+2.49), which was experimentally assigned as 2+.<sup>23</sup> It is also interesting to see that the local charge of Fe in MOF-74-Fe behaves almost like the metallic case, thus increasing the local magnetic moment. The experimental magnetic moment for Co is  $4.67 \mu_B$ ,<sup>23</sup> which is larger than our computed value; a discrepancy connected to the well-known unphysical delocalization of the electron charge density that is introduced by the exchange-correlation functional adopted in DFT simulations.<sup>28</sup> Note that orbital magnetism<sup>29-31</sup> is not included in our calculations, as its effect is typically very small.<sup>32</sup>

Figure 2 shows the density of states of the valence bands projected onto the  $d$ -orbitals of the TM atoms and  $p$ -orbitals of oxygen atoms (pDOS). Here we see that some of the electronic charge density of the TM

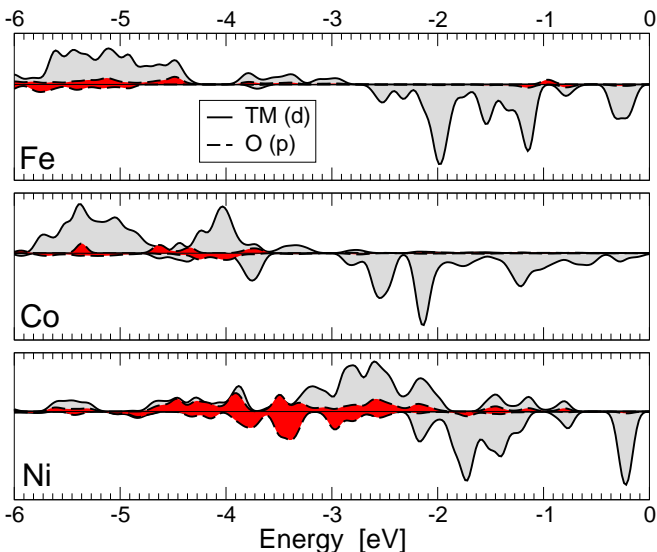


FIG. 2. Projected density of states onto Fe, Co, and Ni  $d$ -orbitals (gray) and O  $p$ -orbitals (red) of the valence bands of MOF-74-TM. Energy is given in eV with respect to the top of the valence band. Spin-up and spin-down densities are plotted above and below the zero line of each plot.

spills-over (due to orbital hybridization) to the nearest-neighbor oxygen atoms. This diminishes the local magnetization on spin-carriers and thus their total magnetic moment. Not surprisingly, the analysis of the pDOS together with the charge analysis suggests that the magnetization originates from the  $d$ -electrons (spin-down, see Fig. 2) of the TM atoms. Note that the angle  $\angle_{\text{TM-O-TM}} \approx 90^\circ \pm 5^\circ$  does not allow sufficient overlap between the relevant orbitals enforcing the intra-chain ferromagnetism according to the Goodenough and Kanamori rules.<sup>33</sup> The above analysis clearly shows how the tunability of the organic linkers in MOFs can be utilized to increase the spin localization on the TM, and a more involved explanation can be found in Ref. 8. From this analysis we conclude the existence of localized magnetic moments that can give rise to ferromagnetic coupling among TM atom chains.

Although we have clarified the existence of chains of spin carriers, we still need to understand if spin chains are independent of each other (see Fig. 1) in order to produce isolated spin arrays acting as linear magnets. To this end, a qualitative estimation of the magnetic independence of spin chains is obtained by performing calculations where each chain magnetization is assigned a random spatial starting orientation, which thereafter is free to relax towards the most favorably energetic orientation. If there is some degree of inter-chain interaction, each chain spin-magnetization will assume some preferred orientation. But, our results show that only a small rearrangement of the spin directions occurs, i.e. only  $\pm 2^\circ$  from the initial directions, supporting the idea that chains are only weakly coupled. However, a quantitative measurement of such chain-chain interactions can only be obtained by

TABLE II. Intra-chain  $J$ -coupling constants  $J_{\text{NN}}$  and  $J_{\text{NNN}}$  and inter-chain  $J_{\text{I-I}}$  for MOF-74-TM in  $\text{cm}^{-1}$ . For clarity we report again the magnetic moment,  $\mu$ , in  $\mu_B$ , from Table I. The standard deviation of  $J_{\text{NN}}$  and  $J_{\text{I-I}}$  is not reported because below the accuracy limit.

TM	$\mu$	$J_{\text{NN}}$	$J_{\text{NNN}}$	$J_{\text{I-I}}$
Fe	3.625	$28.1 \pm 0.4$	6.0	-1.2
Co	3.255	$40.1 \pm 2.9$	4.9	-1.9
Ni	1.567	$21.0 \pm 3.5$	6.9	-1.3

calculating the inter-chain  $J$ -coupling constants, which follows next.

Having established that the TM spin-carriers exhibit a substantial magnetization that can produce potential ferromagnetic coupling, our investigation moves to the calculation of the  $J$ -coupling interactions. Figure 1b shows the magnetic pathways and defines the following  $J$ -couplings: The intra-chain  $J_{\text{NN}}$  and  $J_{\text{NNN}}$ , origin of the 1D linear magnet properties; and, the unwanted inter-chain  $J_{\text{I-I}}$  interactions. A complete structural analysis shows that the intra-chain TM-TM distance falls between 2.8 Å and 3.0 Å for MOF-74-TM, whereas the inter-chain distance falls between 7.5 Å and 8.8 Å, giving reason to believe that the inter-chain  $J$ -coupling interactions are quenched. If each spin magnetization is constrained along the  $z$ -direction,<sup>34</sup> the coupling interaction,  $J_{ij}$ , described by the complex Heisenberg-Dirac-van Vleck Hamiltonian simplifies to the 1D Ising Model<sup>15</sup>

$$\hat{H} = -2 \sum_{i,j}^n J_{ij} \hat{S}_i^z \cdot \hat{S}_j^z, \quad (1)$$

where  $\hat{S}_i^z$  is the projection of the spin operator along the  $z$  direction at site  $i$ . Due to the gyromagnetic factor, for the expectation values of  $\hat{S}_i^z$  we use 1/2 of the magnetic moments  $\mu$  in Table I, i.e. 0.813 for Fe, 1.628 for Co, and 0.784 for Ni. We now use DFT to map the real system onto this model Hamiltonian by computing the energy differences of various ferro- and anti-ferromagnetic spin configurations, which in turn yields the  $J$ -couplings. Our supercell contains 6 independent TM atoms per chain (see Fig. 1b), resulting in  $2^6 = 64$  possible different spin configurations, out of which only 16 combinations are linearly independent and compatible with our periodic boundary conditions. The coupling constants  $J_{ij}$  are then obtained by solving an overdetermined system of 16 equations with a least-square fit. Table II reports our calculated values for the nearest-neighbor coupling  $J_{\text{NN}}$ , the next-nearest-neighbor coupling  $J_{\text{NNN}}$ , and the inter-chain coupling  $J_{\text{I-I}}$  for MOF-74-Fe, MOF-74-Co, and MOF-74-Ni. Note that these calculations are a particularly challenging task requiring high accuracy, as these energy differences are tiny compared to the total energy of a 108 atom unit cell.

From Table II we see that the intra-chain  $J$ -couplings are larger and more positive than the inter-chain ones,

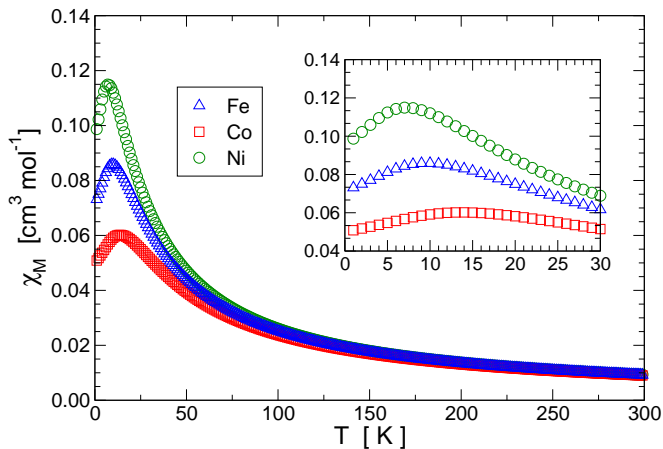


FIG. 3. Computed magnetic susceptibility  $\chi_M$  (in  $\text{cm}^3 \text{mol}^{-1}$ ) as a function of temperature  $T$  (in K) for MOF-74-Fe, MOF-74-Co, and MOF-74-Ni. The inset shows an enlargement of the transition zone.

suggesting the existence of linear ferromagnetism. On the other hand, the interaction among chains is very small and of anti-ferromagnetic nature. As expected, longer range  $J$ -coupling interactions, such as  $J_{\text{NN}}$ , are of smaller magnitudes than the nearest-neighbor interactions and are expected to vanish at increasing distances. Although couplings for longer distances are in principle easily obtainable from Eq. (1), such results are not presented here since they fall below our accuracy limit. Overall, the trend of the magnetic constants is maintained between the three TMs. From our simulations the computed  $J_{\text{NN}}$  for MOF-74-Fe seems largely overestimated from the experimental value of  $4.12 \text{ cm}^{-1}$ , which was extrapolated by fitting experimental magnetic susceptibility profiles.<sup>24</sup> On the other hand, our calculated inter-chain constant for MOF-74-Fe is in excellent agreement with the experimental result of  $-1.12 \text{ cm}^{-1}$ .<sup>24</sup> In summary, we conclude that the ferromagnetic intra-chain interactions are one order of magnitude larger than the anti-ferromagnetic inter-chain ones—confirming the possibility of the existence of 1D-magnetic phenomena at low temperature.

We finally move to calculating the temperature-dependent magnetic susceptibility  $\chi_M$ . Starting from our computed  $J$ -coupling constants, we can predict the magnetic susceptibility,  $\chi_M$ , which is measurable experimentally. We use Fisher’s model<sup>35</sup>

$$\chi_M = \frac{N g_{\text{iso}}^2 \mu^2}{12 k_b T} \times \frac{1 + u(J_{\text{NN}})}{1 - u(J_{\text{NN}})}, \quad (2)$$

$$u(J_{\text{NN}}) = \coth\left(\frac{k_b T}{2 J_{\text{NN}}}\right) - \left(\frac{2 k_b T}{J_{\text{NN}}}\right), \quad (3)$$

where  $N$  is the number of atoms in the chain,  $g_{\text{iso}}$  the  $g$ -factor,  $k_b$  the Boltzman constant, and  $T$  the temperature. Figure 3 shows our calculated  $\chi_M$  as a function of temperature for the three MOF-74-TM investigated, using the  $J_{\text{NN}}$ -coupling constants from Table II. The

transition temperature corresponding to the phase transition from ferromagnetic order to anti-ferromagnetic order along the chains is given by the peak position of  $\chi_M$ . Obviously, the transition temperature depends on the  $J$ -coupling strength: the larger the  $J$ -coupling constant is, the broader the peak becomes and the higher the transition temperature. A similar dependence is found for the  $\chi_M$  magnitude itself, which decreases for increasing  $J$ -coupling constant. For MOF-74-Co, the temperature dependence of  $\chi_M$  was measured experimentally,<sup>23</sup> finding a transition temperature of 8–10 K, in good agreement with our calculated transition temperature of 13 K. The experimental maximum of the peak is at  $\sim 0.17 \text{ cm}^3 \text{mol}^{-1}$ , whereas our calculated maximum is only at  $\sim 0.06 \text{ cm}^3 \text{mol}^{-1}$ . However, this discrepancy is a result of the fact that our DFT calculated Co dipole moment of  $3.255 \mu_B$  is too small compared to the experimental one of  $4.67 \mu_B$  (as mentioned above).<sup>23</sup> As can be seen from Eq. (2) the dipole moment  $\mu$  enters the susceptibility as  $\mu^2$ . If we simply use the experimental dipole value, our peak maximum would be at  $\sim 0.13 \text{ cm}^3 \text{mol}^{-1}$ , in reasonable agreement with experiment. Furthermore, note that according to the susceptibility model used, the  $J_{\text{NN}}$  coupling constant for MOF-74-Fe has to be larger than the  $4.12(6) \text{ cm}^{-1}$  found experimentally through fitting data by Bloch *et al.*;<sup>24</sup> such a small value results in a transition temperature too close to 0 K and below the experimental conditions reported in their study (2–300 K). Equation (2) includes only the effect of  $J_{\text{NN}}$ , making this model quite unsatisfactory. The effect introduced by interchain  $J_{\text{I-I}}$  coupling constant in  $\chi_M$  can be reintroduced in Eq. (3) by replacing  $u(J_{\text{NN}})$  with  $u(|J_{\text{NN}}/J_{\text{I-I}}|)$ , with the effect of slightly shifting all curves by  $\sim -3 \text{ K}$ , bringing them in very good agreement with experimental observation. Our estimated transition temperatures of all three investigated MOFs are clearly above the liquid He temperature, encouraging further experiments on linear magnetism phenomena in MOF-74.

In summary, we have explored the existence of linear magnetic phenomena in the metal organic framework materials MOF-74-Fe, MOF-74-Co, and MOF-74-Ni by using DFT calculations. Our results provide an understanding of the origins and magnitude of linear magnetic effects in these materials. We verify the existence of intra-chain ferromagnetism and quenched anti-ferromagnetic coupling between chains, large enough to be observed at liquid He temperatures. The significance of our finding is that MOF-74 is easily synthesized, safe, and inexpensive. As such, it is likely to be the simplest realization of the 1D Ising model in nature and has the potential to provide simple means to study linear magnetism. Note that the MOFs studied here have not been tailored in any way to make them good 1D magnets. In view of the high tailorability and tunability of MOFs, exciting new opportunities open up, where especially designed linkers and spin-centers decrease the spin-density delocalization and maximize the spin moments, resulting in larger  $J$ -couplings and higher transition temperatures.

This work was entirely supported by the Department of Energy Grant No. DE-FG02-08ER46491.

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  - <sup>34</sup> We have considered the more general case of truly non-collinear spin, but our results show that all three MOF-74 systems indeed prefer collinear spin arrangements. We thus constrain our calculations here to spin directions only along the  $z$ -axis.
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