When metal organic frameworks turn into linear magnets

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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 quasilinear 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 one-dimensional (1D) magnets at low temperature. The interchain coupling is found to be antiferromagnetic, 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.

I. INTRODUCTION

The continued quest for the development of nonvolatile 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.[1–14] Considerable emphasis has been given to the synthesis and prediction of materials showing monodimensional magnetism,[1–14] also referred to as *one-dimensional* (1D) or *linear* magnetism. While 1D magnetism can be explained with the well-understood Ising model (dating back to 1925),[15] 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[8,10,14] or dangerous[9] to synthesize, synthetic inorganic materials and polymers. Although, for example, $CrSb_2$ is one of the few materials that shows naturally 1D antiferromagnetism, this property remains difficult to control and tune.[14] 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.[15,16] 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 difficulties in engineering good model systems exhibiting 1D magnetism are[2,10] (i) finding materials that have quasi-1D chains of spins with significant interactions and large magnetic anisotropy, (ii) finding materials with a large ratio between intra- and interchain magnetic interactions, (iii) finding materials in which ferromagnetism is preserved at "reasonable" low temperatures, (iv) finding materials with very few impurities, which tend to destroy ferromagnetism, and, finally, (v) finding materials that are simple, safe, and 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 $Sr_2Cu(PO_4)_2$, Sr_2CuO_3,[4] and $BaCo_2V_2O_8$,[11] along with nonperiodic magnetic clusters or molecular magnets.[10] Another strategy is the combination of organic molecules and transition metals (TM) to form regular polymer 1D magnets.[2,8,10,13] 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.[2,8,10]

We propose here that metal organic frameworks (MOFs), a novel class of nanoporous 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.[17–20] 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.[17–22] 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.[23] From Fig. 1 it is apparent that MOF-74-TM (with TM = Mn, Fe, Co, Ni, and Cu) can be seen as a 1D magnet since it displays regular pseudochains of transition metals aligned along the basal plane. The helicoidal chains resulting from the atomic motif of Fig. 1(a) are interspaced by "long" organic linkers, suggesting that the interchain interactions are quenched. In fact, MOF-74 shows a large structural ratio (∼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.

II. METHOD

To elucidate the 1D-like magnetic properties exhibited by MOF-74, we study the three isostructural materials, MOF-74-Fe,[24] MOF-74-Co,[23] and MOF-74-Ni.[25] To this end, we use density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) functional, as implemented in QUANTUMESPRESSO.[26] We employ ultrasoft pseudopotentials with wave-function and density cutoffs of 680 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 $2 \times 2 \times 2$
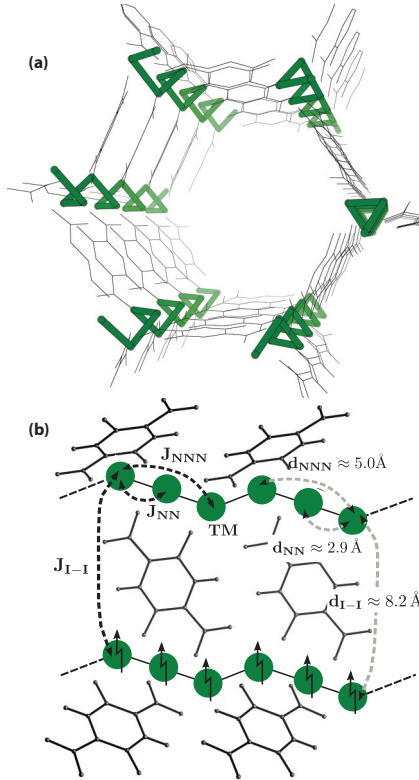
FIG. 1. (Color online) (a) Frontal view of MOF-74; helicoidal magnet chains are highlighted in green. (b) Side view of MOF-74; TM atoms are represented by green balls. d_{NN} and d_{NNN} are the nearest-neighbor and next-nearest-neighbor intrachain distances, while d_{I-I} is the interchain distance. The couplings J_{NN}, J_{NNN}, and J_{I-I} are defined in parallel.

k-point mesh, resulting in energy differences converged to within less than 1 meV. Projected density of states onto selected atomic orbitals is performed on a denser k-point mesh, i.e., $4 \times 4 \times 4$. The SCF total energy convergence criterium is 1.4×10^{-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,[24] MOF-74-Co,[23] and MOF-74-Ni,[25] which crystallize in a rhombohedral primitive cell with 54 atoms and space group $R\bar{3}$. The calculation of the intrachain 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 Supplemental Material.[27]

III. RESULT AND DISCUSSION

A. Density of states and magnetic moments

Linear magnetism relies on ferro- or antiferromagnetism that can only exist if the TM atoms have a non-negligible mag-

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 μ are reported in units of μ_B.

TM	Q_O	$q_O(2p)$	Q_{TM}	$q_{TM}(3d)$	μ
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

netic moment. We therefore begin by analyzing the localization of the magnetic moment on the TM atoms, combining the projected density of states and the Lödwin population analysis. The Lödwin analysis, similar to the Mulliken analysis, is an intuitive (but not unique) way of repartitioning the electron charge density on each atom (and orbital) by projecting it onto individual orthonormalized atomic orbitals.[28] Table I shows the Lödwin charges, relative contribution, and magnetic moments of the TM and O atoms in the three MOF-74 investigated. The magnetic moments μ were computed by integrating the spin-density 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 moments of the TM in MOFs. We further confirm the local charge of Co in MOF-74-Co $(+2.49)$, which was experimentally assigned as $2+$.[23] 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 μ_B,[23] 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.[29] Note that orbital magnetism[30–32] is not included in our calculations, as its effect is typically very small.[33]

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 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 $\angle_{TM-O-TM} \approx 90° \pm 5°$ does not allow sufficient overlap between the relevant orbitals enforcing the intrachain ferromagnetism according to the Goodenough and Kanamori rules.[34] 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
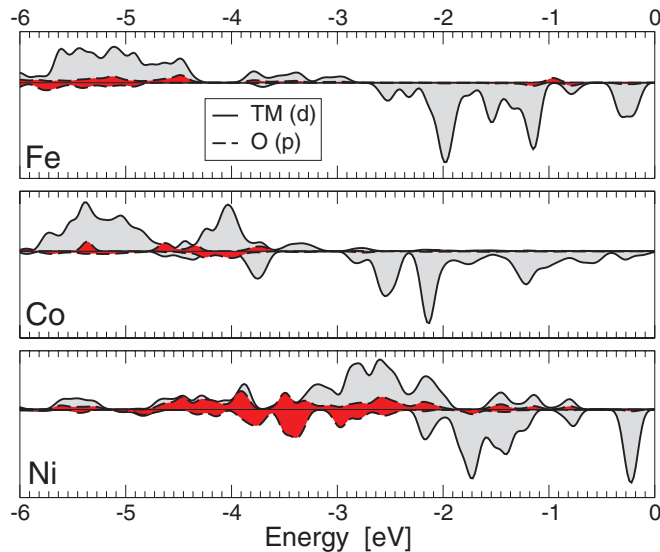
FIG. 2. (Color online) Projected density of states onto Fe, Co, and Ni d orbitals (gray) and O p orbitals (red) of the valence bands of MOF-74-TM. Energy is given in eV with respect to the top of the valence band. Spin-up and spin-down densities are plotted above and below the zero line of each plot.

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 interchain 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 $\pm 2°$ 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 calculating the interchain J-coupling constants, which follows next.

B. J-Coupling interactions

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 1(b) shows the magnetic pathways and defines the following J couplings: the intrachain J_{NN} and J_{NNN}, the origin of the 1D linear magnet properties, and the unwanted interchain J_{I-I} interactions. A complete structural analysis shows that the intrachain TM-TM distance falls between 2.8 and 3.0 Å for MOF-74-TM, whereas the intrachain distance falls between 7.5 and 8.8 Å, giving us reason to believe that the interchain J-coupling interactions are quenched. If each spin magnetization is constrained along the z direction,[35] the coupling interaction J_{ij} described by the complex Heisenberg–Dirac–van Vleck Hamiltonian simplifies to the 1D Ising model,[15]

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

TABLE II. Intrachain J-coupling constants J_{NN} and J_{NNN} and interchain J_{I-I} for MOF-74-TM (in cm^{-1}). For clarity we report again the magnetic moment μ (in units of μ_B) from Table I. The standard deviation of J_{NN} and J_{I-I} is not reported because it is below the accuracy limit.

TM	μ	J_{NN}	J_{NNN}	J_{I-I}
Fe	3.625	28.1 ± 0.4	6.0	-1.2
Co	3.255	40.1 ± 2.9	4.9	-1.9
Ni	1.567	21.0 ± 3.5	6.9	-1.3

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 half of the magnetic moments μ 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 antiferromagnetic spin configurations, which in turn yield the J couplings. Our supercell contains six independent TM atoms per chain [see Fig. 1(b)], 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-squares fit. Table II reports our calculated values for the nearest-neighbor coupling J_{NN}, the next-nearest-neighbor coupling J_{NNN}, and the interchain coupling J_{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 intrachain J couplings are larger and more positive than the interchain ones, suggesting the existence of linear ferromagnetism. On the other hand, the interaction among chains is very small and of antiferromagnetic nature. As expected, longer-range J-coupling interactions, such as J_{NNN}, 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_{NN} for MOF-74-Fe seems largely overestimated from the experimental value of 4.12 cm^{-1}, which was extrapolated by fitting experimental magnetic susceptibility profiles.[24] On the other hand, our calculated interchain constant for MOF-74-Fe is in excellent agreement with the experimental result of -1.12 cm^{-1}.[24] In summary, we conclude that the ferromagnetic intrachain interactions are one order of magnitude larger than the antiferromagnetic interchain ones, confirming the possibility of the existence of 1D magnetic phenomena at low temperature.

C. Magnetic susceptibility χ_M

We finally move to calculating the temperature-dependent magnetic susceptibility χ_M. Starting from our computed J-coupling constants, we can predict the magnetic susceptibility
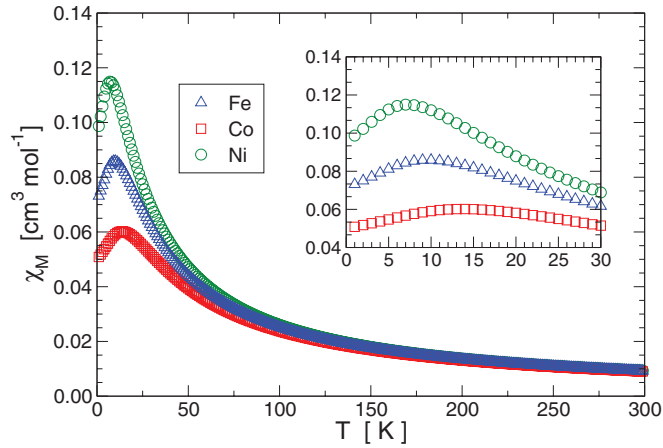
FIG. 3. (Color online) Computed magnetic susceptibility χ_M (in cm^3 mol^{-1}) as a function of temperature T (in K) for MOF-74-Fe, MOF-74-Co, and MOF-74-Ni. The inset shows an enlargement of the transition zone.

χ_M, which is measurable experimentally. We use Fisher's model,[36]

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

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

where N is the number of atoms in the chain, g_{iso} the g factor, k_b is the Boltzmann constant, and T is the temperature. Figure 3 shows our calculated χ_M as a function of temperature for the three MOF-74-TM investigated, using the J_{NN}-coupling constants from Table II. The transition temperature corresponding to the phase transition from ferromagnetic order to antiferromagnetic order along the chains is given by the peak position of χ_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 transition temperature is. A similar dependence is found for the χ_M magnitude itself, which decreases for an increasing J-coupling constant. For MOF-74-Co, the temperature dependence of χ_M was measured experimentally,[23] revealing 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 cm^3 mol^{-1}, whereas our calculated maximum is only at $\sim$0.06 cm^3 mol^{-1}. However, this discrepancy is a result of the fact that our DFT-calculated Co dipole moment of 3.255 μ_B is too small compared to

the experimental one of 4.67 μ_B (as mentioned above).[23] As can be seen from Eq. (2), the dipole moment μ enters the susceptibility as μ^2. If we simply use the experimental dipole value, our peak maximum would be at $\sim$0.13 cm^3 mol^{-1}, in reasonable agreement with experiment. Furthermore, note that according to the susceptibility model used, the J_{NN} coupling constant for MOF-74-Fe has to be larger than the value of 4.12(6) cm^{-1} found experimentally through fitting data by Bloch *et al.*;[24] 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_{NN}, making this model quite unsatisfactory. The effect introduced by the interchain $J_{\text{I}-\text{I}}$ coupling constant in χ_M can be reintroduced in Eq. (3) by replacing $u(J_{\text{NN}})$ with $u(|J_{\text{NN}}/J_{\text{I}-\text{I}}|)$, with the effect of slightly shifting all curves by $\sim$−3 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.

IV. CONCLUSIONS

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 intrachain ferromagnetism and quenched antiferromagnetic 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.

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[27]See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.87.094407 for the atomic coordinates and relative lattice parameters of the supercell structures employed in this study. The matrix transformation used to produce such supercell structures is also reported.

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