Molecular discovery of half-metallic one-dimensional metal-organic framework

Cite as: J. Appl. Phys. **125**, 142906 (2019); <https://doi.org/10.1063/1.5079421>

Submitted: 30 October 2018 . Accepted: 23 January 2019 . Published Online: 28 March 2019

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Junxian Liu, Jian Kang, and Yun Wang^{a)}

AFFILIATIONS

Centre for Clean Environment and Energy, School of Environment and Science, Griffith University, Gold Coast Campus, Queensland 4222, Australia

^{a)}Author to whom correspondence should be addressed: yun.wang@griffith.edu.au

ABSTRACT

The metal-organic framework (MOF) is a large family of nanomaterials with tunable structural and electronic properties. Discovering half-metallic MOF can broaden the selection pool of half-metals for specific applications in the areas of electronics and catalysis. In this study, seven one-dimensional first-row transition metal-dithiolene MOFs have been systematically investigated using the first-principles density functional theory method. Our theoretical outcomes reveal that the electrical conductivities of these MOFs are determined by the electronic configurations of the metal cations. They can change from a semiconductor to a half-metal and further to a metal as the atomic number increases. Among all MOFs we considered, Cr(III)/Mn(III)/Fe(III)/Co(III)-dithiolene MOFs are promising candidates for spintronic applications.

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I. INTRODUCTION

The control of spin degrees of freedom of materials has attracted great interest since it is a promising nanotechnology for advanced spintronic applications, e.g., next-generation data storage, computing-technology devices, and spin catalysis.^{1–8} The main challenge is to manipulate the small spin texture and efficiently utilize it. Half-metallic materials, in which one of its spin directions is metallic while the other spin direction is semiconducting or insulating, have been considered as important candidates for engineering spin degrees of freedom. Half metal was first predicted in 1983⁹ and has greatly developed recently.^{10–13} Given the high cost of the experimental fabrication and characterization of materials, the establishment of the candidate pool based on high-accuracy computations is a more efficient and economic approach to discover novel half-metals. Indeed, theoretical studies have predicted the existence of a series of half-metals^{14–18} and some of them were experimentally confirmed later.¹⁹

The metal-organic frameworks (MOFs), which are made by linking metal nodes with organic ligands through strong bonds, have many potential applications in the fields of nanoscience and nanotechnology since they offer specific advantages owing to tunable pore metrics for ion transport, tunable electronic properties, high surface areas, high density of active catalytic sites, and quantum size effect.^{20–22}

Most of the traditional MOFs are insulators or semiconductors. However, the electrical conductive MOFs have been synthesized and applied in electrocatalysis and sensing,²³ which indicates that the electronic properties of MOFs can be well tuned by adjusting their inorganic and organic components. As such, previous studies open the door to develop half-metallic MOFs for spintronic applications through the manipulation of properties of MOFs. Yet, studies on the half-metallic MOFs are still at a fledging stage.

Recently, one-dimensional (1D) cobalt(III)-dithiolene MOFs have been successfully synthesized and demonstrated to possess high electrical conductivity with considerably high thermal and dynamic stability.^{24,25} Soon, other transition metal-dithiolene MOFs have also been synthesized,²⁶ which demonstrate the capability of synthesis of 1D MOFs with different metal nodes. Thus, it provides the opportunity to discover half-metallic low-dimensional materials from this class of 1D MOFs.

In this study, seven types of 1D first-row TM-dithiolene MOFs (TM = Ti, V, Cr, Mn, Fe, Co, or Ni) were systematically investigated using the first-principles density functional theory (DFT). We investigated their electrical conductivities based on their electronic structures, electron localization function (ELF),²⁷ and Bader charges.²⁸ The theoretical findings demonstrate that the 1D TM-dithiolene MOFs change from a semiconductor to a half-metallic and further

to metallic materials with the increase of the atomic number of the first-row TM in the periodic table.

II. COMPUTATIONAL DETAILS

All spin-polarized theoretical computations were performed using the DFT within the Vienna Ab Initio Simulation Package (VASP) code in this study.^{29–31} Ion-electron interactions were described using the projected augmented wave (PAW)³² potentials, with valence configurations of $3s^2 3p^6 4s^2 3d^2$ for Ti (Ti_sv_GW), $3s^2 3p^6 4s^2 3d^3$ for V (V_sv_GW), $3s^2 3p^6 4s^2 3d^4$ for Cr (Cr_sv_GW), $3s^2 3p^6 4s^2 3d^5$ for Mn (Mn_sv_GW), $3s^2 3p^6 4s^2 3d^6$ for Fe (Fe_sv_GW), $3s^2 3p^6 4s^2 3d^7$ for Co (Co_sv_GW), $3s^2 3p^6 4s^2 3d^8$ for Ni (Ni_sv_GW), $3s^2 3p^4$ for S (S_GW), $2s^2 2p^2$ for C (C_GW_new), and $1s^1$ for H (H_GW). For the exchange-correlation functional, the generalized gradient approximation (GGA) level with the format of Perdew-Burke-Ernzerhof (PBE) was used.³³ A plane-wave basis set with a cutoff kinetic energy of 520 eV was employed to expand the smooth part of wave functions.

The 1D TM-dithiolene MOF was modeled with a supercell, which is periodic along the x direction and separated by vacuum layers of 15 Å in the y and z directions, respectively, as shown in Fig. S1 in the [supplementary material](#). Each unit cell includes one first-row TM cation, four S atoms, six C atoms, two H atoms, and one unit of the negative charge, which was set based on the experimental observations by Downes *et al.*²⁴ When the geometries of 1D MOFs were optimized, all the atoms were allowed to relax until Hellmann-Feynman forces were smaller than 0.01 eV/Å and the convergence criterion for the electronic self-consistent loop was set to 1×10^{-5} eV. For the structural optimization and analyses of electronic properties, we performed Brillouin zone integrations using the gamma-centered ($8 \times 1 \times 1$) and ($40 \times 1 \times 1$) k -point grids, respectively. Considering the Coulomb repulsion between the localized d -electrons of transition metals, the GGA + U approach was used with U–J values of 4.3, 3.4, 3.2, 3.5, 4.3, 4.0, and 5.5 eV for Ti, V, Cr, Mn, Fe, Co, and Ni, respectively. The U–J values were selected from the work of Carter *et al.*, who adopted an *ab initio* approach to generate these values.^{34–40}

III. RESULTS AND DISCUSSION

To figure out the most stable geometric and electronic structures of these 1D TM-dithiolene MOFs, we optimized the structures by considering all possible electronic configurations of TM cations. Figure 1(a) gives the atomic geometry of the TM-dithiolene MOFs. Here, the z axis is along the normal of the 1D planar MOFs, and the x axis is along the 1D MOF direction. On the basis of the crystal field theory, the 3d orbitals of metals split into three groups due to the impact from the ligands with the square-plane symmetry and the D2h point group. d_{z^2} and $d_{x^2-y^2}$ have the lowest energy level, followed by d_{xz} and d_{yz} . d_{xy} has the highest energy level, as demonstrated by the previous theoretical study on the Co(III)-dithiolene monoanion.⁴¹ The electrons can occupy the 3d orbitals with different electronic configurations in terms of the splitting energy of the orbitals.^{42,43} As such, there are different electronic configurations for Cr(III), Mn(III), Fe(III), Co(III), and Ni(III)/Ni(II), which lead to different spin states and magnetic moments [see Figs. 1(b)–1(h)]. It is noted that there is a Ni(III) $\leftrightarrow$ Ni(II) transformation due to the

existence of the resonance structure through the interaction between the ligands and the cations in the 1D nickel-dithiolene MOF. Thus, there is a spin state of 0.0 μ_B /unit for the Ni(II)-based MOF [see Fig. 1(h)]. The details about the Ni(III) $\leftrightarrow$ Ni(II) transformation will be discussed in detail in subsequent analyses.

The structural optimization results reveal that the 1D MOFs keep the planar geometry with the D2h point group. Their structural and energetic properties with the possible spin states of TM cations are listed in Table I. Our results demonstrate that the spin state of TM(III) cations significantly affects the energy of the most stable structures. For the Ti(III) and V(III)-dithiolene MOFs, there is only one possible spin state. As evidenced by Table I, the high-spin states of Cr(III) (3.0 μ_B /unit) and Mn(III) (4.0 μ_B /unit) are more thermodynamically favored in the 1D MOF. Fe(III) has three possible spin states with magnetic moments of 1.0, 3.0, and 5.0 μ_B /unit, respectively. The spin state with the magnetic moment of 3.0 μ_B /unit is the most stable electronic configuration. The Co(III) is thermodynamically stable at a low-spin state (2.0 μ_B /unit) in the MOF, which is consistent with previous experimental and theoretical conclusions that the triplet is more thermodynamically preferred.⁴⁴ The preference of the spin states of different TM cations suggests that the splitting energies between the low-energy 3d orbitals (d_{z^2} and $d_{x^2-y^2}$) and the middle-energy orbitals (d_{xz} and d_{yz}) are small. As a result, the high-spin states of Cr(III) and Mn(III) are more stable than their low-spin states. As a comparison, the splitting energy between the middle-energy 3d orbitals and the high-energy d_{xy} orbital is so large that the spin-states of Fe(III) and Co(III) with the unoccupied d_{xy} orbital are more energetically preferred.

Surprisingly, Ni cation in the 1D MOF prefers to thermodynamically stabilize at the spin state with a magnetic moment of 0.0 μ_B /unit. Based on the electronic configuration of Ni(III), its lowest spin state possesses a magnetic moment of 1.0 μ_B /unit. The stable singlet state suggests the existence of Ni(II) cations. In regard to the electronic structure of the square-planar monoanionic complex $[M(L)_2]^{1-}$, the mixed metal-ligand character frontier states in the 1D M(III)-dithiolene MOF make it complicated to identify the exact oxidation states of transition metal cations in these MOFs. A recent study indicated the existence of multiple oxidation states in the low-dimensional cobalt-dithiolene MOF and the resonance forms of $[Co(III)(L^{2-})(L^{2-})]^- \leftrightarrow [Co(II)(L^{\cdot-})(L^{2-})]^-$, while $[Co(III)(L^{2-})(L^{2-})]^-$ is the dominant state.⁴¹ Here, L represents the dithiolene ligand. Our results, therefore, suggest that $[Ni(II)(L^{\cdot-})(L^{2-})]^-$ is more energetically preferred in this type of 1D MOFs. This can be understood because the four 3d orbitals with the lower energy level of Ni(II) are fully occupied with a magnetic moment of 0.0 μ_B /unit, which can stabilize the $[Ni(II)(L^{\cdot-})(L^{2-})]^-$ state.

The impact of the different magnetic moments along the neighboring units is also considered here. To investigate the antiferromagnetic (AFM) structure, the unit cell is doubled along the x direction with two TM cations. The major spin component of each TM cation has a different direction. The energy difference between the AFM and the FM structures is listed in Table S1 in the [supplementary material](#). Here, it is found that most of the 1D TM-dithiolene MOFs, except Cr, with AFM structures are less than 15 meV/unit more stable than that with FM structures. The considerably weak magnetic coupling can be ascribed to the long distance between the neighboring metal cations (>8 Å, see Table I). Since

FIG. 1. (a) The atomic configuration of the 1D TM(III)-dithiolene MOFs, TM = Ti, V, Cr, Mn, Fe, Co, or Ni. The red dotted box shows a unit cell. Yellow, sulfur; brown, carbon; and white, hydrogen; (b)–(h) Electronic configurations of TM(III) in 1D MOFs and the corresponding magnetic moment per unit cell in μ_B .

$1 \kappa_B T$ is about 25 meV at room temperature, the small energy differences suggest that the long-range AFM ordering may not be kept under the mild condition. The FM state with the smaller unit cell, therefore, can be used to save the computational time and be further studied.

The calculated lattice constants along the periodic table decrease, while the calculated TM–S bond lengths also gradually decrease from Ti to Ni (see Fig. S2 in the [supplementary material](#)). Their change trends are strongly relevant to the trend of the radii of their cations in the periodic table. The radii of first-row TM

atoms will decrease with the increase of the atomic number due to the increased protons. The ELF images (see Fig. 2) suggest that the nature of TM–S bonds is ionic since there is no shared electron density between them.²⁷ The change in the length of the ionic bonds can, therefore, be ascribed to the change of the radii of the TM cations, which can affect the corresponding lattice constants.

The Bader charge of TM and S ions, which is shown in Fig. 3, was calculated to analyze the electronic properties of the 1D MOFs. The result reveals that the TM cations lose less electrons as the atomic number increases. Accordingly, the S atoms gain less electrons

TABLE I. Spin states (μ_B), lattice constant (L , Å), TM-S bond length ($d_{\text{TM-S}}$, Å), and the total energy of each unit (E , eV) of 1D TM-dithiolene MOFs with different spin states. The properties of the thermodynamically most stable species are highlighted using boldface.

TM	Spin state (μ_B)	L	$d_{\text{TM-S}}$	E
Ti	1	9.03	2.43	-89.89
V	2	8.88	2.35	-90.25
Cr	1	8.79	2.26	-89.05
	3	8.85	2.35	-90.47
Mn	0	8.68	2.21	-87.80
	4	8.80	2.32	-90.11
Fe	1	8.70	2.25	-86.98
	3	8.70	2.25	-87.56
	5	8.80	2.36	-87.04
Co	2	8.62	2.20	-86.18
	4	8.81	2.36	-85.43
Ni	0	8.54	2.18	-83.71
	1	8.57	2.18	-83.58
	3	8.70	2.32	-83.08

from TM when the TM becomes heavier. This can be ascribed to the change of the electronegativity of TM, which gradually increases from Ti to Ni (except Mn due to its half-fill $3d$ feature). The smaller electronegativity value suggests a stronger capability of losing electrons of particles. As such, less charge densities of the TM atoms are lost with the increase of their atomic number after the formation of TM-S ionic bonds within 1D MOFs.

To evaluate the electrical conductivity of 1D TM-dithiolene MOFs, their density of states (DOS) were calculated by considering the spin polarizations. Figure 4 shows that the electronic structures of different TM ions significantly change. As shown in Figs. 4(a) and 4(b), the total DOS of both spin components of Ti(III)-/V(III)-dithiolene MOFs are zero at the Fermi level with bandgap energies of 1.01 and 0.69 eV, respectively, indicating the semiconducting behaviors in both spin directions. As a comparison, there

FIG. 3. The diagram of electronegativity of TM (black triangle) and the corresponding transferred.

is a selectivity of spin orientation for the electronic structures of Cr-S, Mn-S, Fe-S, and Co-S MOFs, which indicates that they are half-metals [see Figs. 4(c)-4(f)]. For the spin-up state, these MOFs are metallic, while they are semiconductors in terms of their spin-down states. Interestingly, the Ni-S MOFs possess metallic properties in both two spin directions. The electronic structures of different 1D TM-dithiolene MOFs are also confirmed by their band structures, as shown in Fig. 5.

To understand the origin of the change of the electronic structures of 1D TM-dithiolene MOFs, the partial DOS of their frontier states, e.g., S $3p_z$, TM $3d_{xz}$, $3d_{yz}$, and $3d_{xy}$, are calculated and shown in Fig. 6. The TM $3d_{z^2}$ and $3d_{x^2-y^2}$ states are not shown here since d_{z^2} and $d_{x^2-y^2}$ locate at the lowest energy level in the square-planar

FIG. 2. The electron localization functions of 1D TM-dithiolene MOFs. (a) Ti; (b) V; (c) Cr; (d) Mn; (e) Fe; (f) Co; and (g) Ni.

FIG. 4. The total DOS of the 1D TM (III)-dithiolene MOFs.

FIG. 5. The band structures of the 1D TM(III)-dithiolene MOFs.

field. As such, both states are in the bonding area and their energies are far from the Fermi energy level without direct impact on their electronic structures. For Ti and V [see Figs. 6(a)–6(b)], the main component of the valence band maximum (VBM) is from the S

$3p_z$ state, and the Ti/V $3d_{xz}$ and $3d_{yz}$ states are the main components of their conduction band minimum (CBM). This is in agreement with the electronic configuration of these two trivalent cations. Since the S $3p_z$ state is fully occupied and the CBM is fully

FIG. 6. The partial DOS of the 1D TM (III)-dithiolene MOFs.

empty, as such, the semiconductor behaviors have been observed in these two MOFs. For other TMs, d_{yz} and d_{xz} states locate at the non-bonding area around the Fermi energy level since they have been partially occupied (see Fig. 1). For the most stable spin

configuration of the Cr(III)-Co(III) cations, the non-bonding d_{yz} and d_{xz} states are occupied by electrons only with the same spin direction. Consequently, these materials show the half-metallic characteristics. Dissimilarly, in the most stable 1D Ni-S MOFs with

the $[\text{Ni}(\text{II})(\text{L}^{\bullet-})(\text{L}^{2-})]^-$ state, all bonding orbitals and non-bonding $3d$ states are fully occupied, leading to the metallic characteristics at both spin orientations.

IV. CONCLUSIONS

In summary, our first-principles DFT calculations were performed to investigate the electronic properties of the 1D first-row TM-dithiolene MOFs. First, the most stable configurations of the MOFs have been identified by considering the possible spin states. The electrons prefer to first occupy the d_{z^2} , $d_{x^2-y^2}$, d_{xz} , and d_{yz} orbitals with the high-spin structure due to a small splitting energy between them. As a comparison, the high energy level of the $3d_{xy}$ orbital leads to the $3d_{xy}$ orbital being unoccupied in the electronic ground state. The analysis based on the electronic structures, ELF, Bader charges, DOS, and band structures demonstrates that the 1D first-row TM-dithiolene MOFs have good electrical conductivities. In addition, changing metal cations with different transition metals in the 1D MOFs can trigger the transition from a semiconductor to a half-metal and to a metal due to their different electronic configurations. Our theoretical results present that the 1D Cr(III)/Mn(III)/Fe(III)/Co(III)-dithiolene MOFs have the desired half-metallic properties. The findings in this study may, therefore, offer the theoretical guidance for the molecular design of half-metals with the low-dimensional MOF structures.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the supercell model, structural properties, and energy difference between different magnetic structures of the 1D TM-dithiolene MOF materials.

ACKNOWLEDGMENTS

This work was supported by the Australian Research Council (No. DP 170104834). This research was undertaken on the supercomputers in the National Computational Infrastructure (NCI) in Canberra, Australia, which is supported by the Australian Commonwealth Government, and the Pawsey Supercomputing Centre in Perth, with funding from the Australian government and the Government of Western Australia.

REFERENCES

- ¹J. Torrejon, M. Riou, F. A. Araujo, S. Tsunegi, G. Khalsa, D. Querlioz, P. Bortolotti, V. Cros, K. Yakushiji, A. Fukushima, H. Kubota, S. Yuasa, M. D. Stiles, and J. Grollier, *Nature* **547**(7664), 428–431 (2017).
- ²S. Parkin and S. H. Yang, *Nat. Nanotechnol.* **10**(3), 195–198 (2015).
- ³A. Fert, V. Cros, and J. Sampaio, *Nat. Nanotechnol.* **8**(3), 152–156 (2013).
- ⁴K. Olejnik, T. Seifert, Z. Kašpar, V. Novák, P. Wadley, R. P. Campion, M. Baumgartner, P. Gambardella, P. Němec, J. Wunderlich, J. Sinova, P. Kužel, M. Müller, T. Kampfrath, and T. Jungwirth, *Sci. Adv.* **4**, 3566–3573 (2018).
- ⁵A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, *Science* **294**(5546), 1488–1495 (2001).
- ⁶A. Ney, C. Pampuch, R. Koch, and K. H. Ploog, *Nature* **425**, 485 (2003).
- ⁷S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, and K. Ando, *Nat. Mater.* **3**(12), 868–871 (2004).
- ⁸S. S. P. Parkin, C. Kaiser, A. Panchula, P. M. Rice, B. Hughes, M. Samant, and S.-H. Yang, *Nat. Mater.* **3**, 862 (2004).
- ⁹R. A. de Groot, F. M. Mueller, P. G. v. Engen, and K. H. J. Buschow, *Phys. Rev. Lett.* **50**(25), 2024–2027 (1983).
- ¹⁰P. Dowben, *J. Phys. Condens. Matter* **19**(31), 310301 (2007).
- ¹¹H. van Leuken and R. A. de Groot, *Phys. Rev. Lett.* **74**(7), 1171–1173 (1995).
- ¹²K. W. Lee and C. E. Lee, *Adv. Mater.* **24**(15), 2019–2023 (2012).
- ¹³I. Galanakis and E. Şaşıoğlu, *Appl. Phys. Lett.* **99**(5), 052509 (2011).
- ¹⁴W.-H. Xie, B.-G. Liu, and D. G. Pettifor, *Phys. Rev. B* **68**(13), 134407 (2003).
- ¹⁵Y.-Q. Xu, B.-G. Liu, and D. G. Pettifor, *Phys. Rev. B* **66**(18), 184435 (2002).
- ¹⁶S. W. Fan, L. J. Ding, Z. L. Wang, and K. L. Yao, *Appl. Phys. Lett.* **102**(2), 022404 (2013).
- ¹⁷S.-W. Fan, W.-B. Li, X.-N. Huang, Z.-B. Li, and L.-q. Pan, *Appl. Phys. Express* **8**(4), 045802 (2015).
- ¹⁸J. Li, Y. Li, G. Zhou, Y. Sun, and C. Q. Sun, *Appl. Phys. Lett.* **94**(24), 242502 (2009).
- ¹⁹J. H. Park, E. Vescovo, H. J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, *Nature* **392**, 794 (1998).
- ²⁰S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao, L. Zhang, J. Lv, J. Wang, J. Zhang, A. M. Khattak, N. A. Khan, Z. Wei, J. Zhang, S. Liu, H. Zhao, and Z. Tang, *Nat. Energy* **1**, 16184 (2016).
- ²¹A. J. Clough, J. W. Yoo, M. H. Mecklenburg, and S. C. Marinescu, *J. Am. Chem. Soc.* **137**(1), 118–121 (2015).
- ²²D. M. D'Alessandro, *Chem. Commun.* **52**(58), 8957–8971 (2016).
- ²³L. Sun, M. G. Campbell, and M. Dinca, *Angew. Chem. Int. Ed.* **55**(11), 3566–3579 (2016).
- ²⁴C. A. Downes and S. C. Marinescu, *J. Am. Chem. Soc.* **137**(43), 13740 (2015).
- ²⁵Y. Wang, X. Liu, J. Liu, M. Al-Mamun, A. W.-C. Liew, H. Yin, W. Wen, Y. L. Zhong, P. Liu, and H. Zhao, *ACS Appl. Energy Mater.* **1**(4), 1688–1694 (2018).
- ²⁶C. A. Downes and S. C. Marinescu, *Dalton Trans.* **45**(48), 19311–19321 (2016).
- ²⁷B. Silvi and A. Savin, *Nature* **371**(6499), 683–686 (1994).
- ²⁸R. F. W. Bader and C. F. Matta, *J. Phys. Chem. A* **108**, 8385–8394 (2004).
- ²⁹G. Kresse and J. Hafner, *Phys. Rev. B* **48**(17), 13115–13118 (1993).
- ³⁰G. Kresse and J. Furthmüller, *Comp. Mater. Sci.* **6**(1), 15–50 (1996).
- ³¹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**(16), 11169–11186 (1996).
- ³²G. Kresse and D. Joubert, *Phys. Rev. B* **59**(3), 1758–1775 (1999).
- ³³J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**(18), 3865–3868 (1996).
- ³⁴P. Liao, M. C. Toroker, and E. A. Carter, *Nano Lett.* **11**(4), 1775–1781 (2011).
- ³⁵K. Chakrapani, G. Bendt, H. Hajiyani, T. Lunkenbein, M. T. Greiner, L. Masliuk, S. Salamon, J. Landers, R. Schlögl, H. Wende, R. Pentcheva, S. Schulz, and M. Behrens, *ACS Cat.* **8**(2), 1259–1267 (2018).
- ³⁶N. J. Mosey, P. Liao, and E. A. Carter, *J. Chem. Phys.* **129**(1), 014103 (2008).
- ³⁷M. Pavone, A. B. Muñoz-García, A. M. Ritzmann, and E. A. Carter, *J. Phys. Chem. C* **118**(25), 13346–13356 (2014).
- ³⁸A. M. Ritzmann, A. B. Muñoz-García, M. Pavone, J. A. Keith, and E. A. Carter, *MRS Commun.* **3**(03), 161–166 (2013).
- ³⁹A. M. Ritzmann, M. Pavone, A. B. Muñoz-García, J. A. Keith, and E. A. Carter, *J. Mater. Chem. A* **2**(21), 8060–8074 (2014).
- ⁴⁰A. J. Tkalych, K. Yu, and E. A. Carter, *J. Phys. Chem. C* **119**(43), 24315–24322 (2015).
- ⁴¹K. Ray, A. Begum, T. Weyhermüller, S. Piligkos, J. van Slageren, F. Neese, and K. Wieghardt, *J. Am. Chem. Soc.* **127**, 4403–4415 (2005).
- ⁴²X. Y. Cui, B. Delley, A. J. Freeman, and C. Stampfl, *Phys. Rev. Lett.* **97**(1), 016402 (2006).
- ⁴³X. Y. Cui, A. Soon, A. E. Phillips, R. K. Zheng, Z. W. Liu, B. Delley, S. P. Ringer, and C. Stampfl, *J. Magn. Magn. Mater.* **324**(19), 3138–3143 (2012).
- ⁴⁴B. H. Solis and S. Hammes-Schiffer, *J. Am. Chem. Soc.* **134**(37), 15253–15256 (2012).