



2014

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Pradhan, K. and Jena, P. LiFe<sub>2</sub>Cl<sub>n</sub> (n = 4–6) clusters: Double-exchange mediated molecular magnets. *Applied Physics Letters*, 105, 163112 (2014). Copyright © 2014 AIP Publishing LLC.

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## LiFe<sub>2</sub>Cl<sub>n</sub> (*n* = 4–6) clusters: Double-exchange mediated molecular magnets

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(Received 5 September 2014; accepted 12 October 2014; published online 24 October 2014)

A systematic study of LiFe<sub>2</sub>Cl<sub>n</sub> (*n* = 4–6) clusters, based on gradient corrected density functional theory (DFT), shows that the electron contributed by Li can transform antiferromagnetic Fe<sub>2</sub>Cl<sub>n</sub> (*n* = 4 and 6) clusters into ferromagnetic clusters. In Fe<sub>2</sub>Cl<sub>6</sub> (Fe<sub>2</sub>Cl<sub>4</sub>) cluster, the Fe atoms in +3 (+2) oxidation states are aligned antiferromagnetically, consistent with the super-exchange model. The extra electron from Li atom creates a charge disproportionation in the LiFe<sub>2</sub>Cl<sub>6</sub> (LiFe<sub>2</sub>Cl<sub>4</sub>) cluster that mediates the double-exchange interaction between the Fe atoms. Antiferromagnetic to ferromagnetic transition can also be induced by hole doping as seen to be the case with Fe<sub>2</sub>Cl<sub>5</sub> which has a ferromagnetic ground state. Simultaneous electron and hole doping is also seen to impact on the magnetic properties of LiFe<sub>2</sub>Cl<sub>5</sub> which can be viewed as (Fe<sub>2</sub>Cl<sub>4</sub>+LiCl). While Fe<sub>2</sub>Cl<sub>4</sub> is antiferromagnetic and LiCl is nonmagnetic, the ground state of LiFe<sub>2</sub>Cl<sub>5</sub> is ferromagnetic. We also analyzed the results with on-site Coulomb interaction *U* by performing DFT+*U* calculations. These results can be useful in the synthesis of functional molecular magnets. © 2014 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4900421>]

The discovery of single molecule magnet in early 1990s<sup>1,2</sup> bridged different disciplines of science<sup>3</sup>—Physics, Chemistry, Biology, and Materials Science. Understanding the origin of magnetism in molecular clusters has since been an active area of research as functional molecular magnets show promise in the areas of spintronics,<sup>4</sup> quantum computing,<sup>5</sup> and storage devices.<sup>6</sup> In molecular systems, magnetic coupling, in general, is governed by super-exchange interactions,<sup>7</sup> which often lead to antiferromagnetic order.<sup>8</sup> Recent theoretical and experimental results show that ferromagnetic (FM) ground states can be achieved via double-exchange<sup>9</sup> interactions in di-nuclear transition metal complexes by charge transfer and/or charge disproportionation between the transition metal (TM) atoms.<sup>10–14</sup> Unlike the direct-exchange interaction, the double-exchange interaction involves spin dependent electron delocalization through non-magnetic atoms, originally proposed for three dimensional transition metal oxides.<sup>15</sup>

In order to illustrate the mechanism necessary to control the magnetic interaction between TM atoms in a single molecular magnet, we focus on di-nuclear TM-based complexes. This work is motivated by an earlier study<sup>16</sup> in which a series of Mn<sub>k</sub>Cl<sub>2k+1</sub> (*k* = 1–3) clusters were found to be superhalogens<sup>17,18</sup> and potential candidates for molecular magnets. The magnetic nature of these Mn<sub>k</sub>Cl<sub>2k+1</sub> clusters originates from the 3*d*<sup>5</sup> configuration of the Mn<sup>+2</sup> ions<sup>19</sup> when interacting with Cl atoms. We note that TM atoms, due to their multivalent nature, not only possess varying oxidation states but also their precise value depends on the electronegativity of the ligands. For example, the preferred oxidation states of Mn atom are +2 and +3 when interacting with Cl and F atoms, respectively. This is due to the larger electronegativity of F compared to Cl for which MnCl<sub>3</sub> is found to be a superhalogen, while MnF<sub>3</sub> is not.<sup>19</sup> It is also important to note that oxidation state of Mn can be as large

as +7 as evidenced in the superhalogen behavior of MnO<sub>4</sub> cluster.<sup>20</sup> Both the neutral and the anionic Mn<sub>2</sub>Cl<sub>5</sub> clusters<sup>16</sup> are found to have antiferromagnetic (AFM) ground states due to the super-exchange interaction between the localized 3*d*<sup>5</sup> electrons. The density functional theory-based calculations show that the ground state magnetic configuration of LiMn<sub>2</sub>Cl<sub>5</sub> cluster, which has similar electronic configuration to that of anionic Mn<sub>2</sub>Cl<sub>5</sub><sup>−</sup> cluster, also has antiferromagnetic spin configuration.<sup>21</sup>

Photoelectron spectroscopy (PES) experiments<sup>22</sup> have revealed that FeCl<sub>3</sub> and FeCl<sub>4</sub> clusters are also superhalogens, which were attributed to the +2 and +3 oxidation states, respectively, of the Fe atoms. Thus, assuming that Fe can maintain its +2 and +3 oxidation states in di-nuclear complexes, one would expect that Fe<sub>2</sub>Cl<sub>n</sub> (*n* = 5–7) clusters can also be superhalogens.<sup>23,24</sup> In this letter, we have explored the possibility that ferromagnetic molecular magnets can be designed by combining the superhalogen concept with the magnetic properties of the di-nuclear complexes. We focus on Fe<sub>2</sub>Cl<sub>n</sub> and LiFe<sub>2</sub>Cl<sub>n</sub> (*n* = 4–6) clusters. We demonstrate that the Fe atoms indeed interact ferromagnetically in the LiFe<sub>2</sub>Cl<sub>n</sub> clusters due to the induced double-exchange interactions brought about by charge disproportionation inherent in the +2 and +3 oxidation states of Fe atoms. We expect that these results will be helpful in synthesizing functional molecular magnets.

Density functional theory (DFT)-based calculations on Fe<sub>2</sub>Cl<sub>n</sub> and LiFe<sub>2</sub>Cl<sub>n</sub> (*n* = 4–6) clusters are carried out using the super-cell approach and plane-wave pseudopotentials, implemented in the VASP code.<sup>25–27</sup> The exchange-correlation potential is treated within the generalized gradient approximation (GGA) using the PW91 functional.<sup>28</sup> Projector augmented wave basis set with an energy cutoff of 500 eV was used. Brillouin zone integrations are carried out using only the gamma point. The ground state geometries of the clusters were optimized without any symmetry constraint using the conjugate gradient method for different spin multiplicities in a

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super-cell (cubic box of sides  $20 \text{ \AA}$ ). Calculations were also performed using GGA+U approach proposed by Dudarev *et al.*<sup>29</sup> for electron correlation effects. These results are discussed in the last part of the paper.

We begin our calculations with  $\text{Fe}_2\text{Cl}_4$  cluster where Fe is expected to be in +2 oxidation state and gradually increased the number of Cl atoms. The +2 oxidation states of Fe atoms (in  $3d^6$  electronic configuration) would allow  $\text{Fe}_2\text{Cl}_4$  to have an AFM ground state if all the  $3d$  electrons in Fe ions were localized. A FM  $\text{Fe}_2\text{Cl}_4$  cluster will exist only if the charge disproportionation between the Fe atoms would result in an itinerant electron to mediate the double-exchange interaction between the Fe ions. On the other hand, the built-in charge disproportionation in  $\text{Fe}_2\text{Cl}_5$  cluster ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) can mediate the double-exchange interaction between the Fe atoms. In  $\text{Fe}_2\text{Cl}_6$ , the Fe atoms in +3 oxidation states are expected to have stable half-filled  $3d^5$  electronic configurations. Thus, based on the super-exchange model, one would expect  $\text{Fe}_2\text{Cl}_6$  to have an AFM ground state, if the direct-exchange interaction between the Fe atoms is not possible.

The ground state geometries of  $\text{Fe}_2\text{Cl}_n$  ( $n=4-6$ ) clusters corresponding to the FM and AFM states are shown in Fig. 1. Both the FM ( $C_{2v}$  symmetry) and AFM ( $D_{2h}$  symmetry) configurations of the  $\text{Fe}_2\text{Cl}_4$  clusters are found to have two bridged and two terminal Cl atoms. In the case of  $\text{Fe}_2\text{Cl}_5$  cluster, the FM configuration ( $D_{3h}$  symmetry) is the ground state geometry that has three bridged and two terminal Cl atoms. In the AFM configuration ( $C_{2v}$  symmetry), on the other hand, there are two bridged and three terminal Cl atoms. There are two bridged and four terminal Cl atoms in both of the FM and AFM configurations (both with  $C_{2v}$  symmetry) in  $\text{Fe}_2\text{Cl}_6$  cluster.

The magnetic moments of Fe atoms are aligned antiferromagnetically in the ground state geometry of  $\text{Fe}_2\text{Cl}_4$  cluster due to the super-exchange interaction. Note that the FM state of  $\text{Fe}_2\text{Cl}_4$  cluster is only 0.04 eV higher in energy than that of the AFM state. The distance between the Fe atoms in the FM state is  $2.41 \text{ \AA}$ , while it is  $2.74 \text{ \AA}$  in the AFM state.

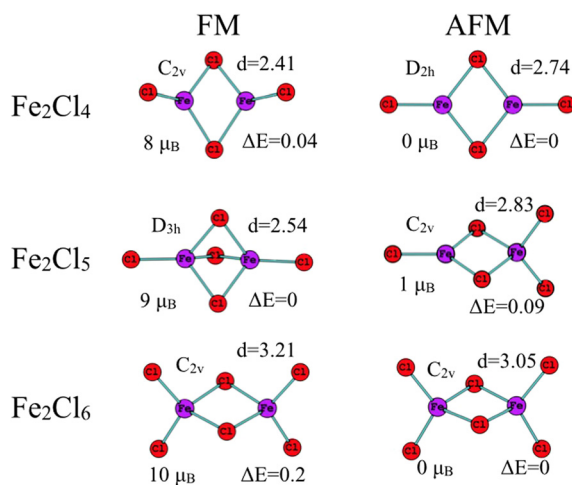


FIG. 1. Optimized ground state geometries of  $\text{Fe}_2\text{Cl}_n$  ( $n=4-6$ ) clusters corresponding to the ferromagnetic and antiferromagnetic states. The relative energies  $\Delta E$  (in eV), magnetic moments (in  $\mu_B$ ) and distance ( $d$ ) between Fe atoms (in  $\text{ \AA}$ ) are also given. The corresponding symmetries are listed.

Due to decrease in the distance between the Fe atoms, one would suspect that the FM state might be due to the direct-exchange interaction between the Fe ions.

To understand the origin of the FM interaction, we plot the one-electron energy levels for FM state of  $\text{Fe}_2\text{Cl}_4$  cluster in Fig. 2(a). The total magnetic moment in the FM state is  $8 \mu_B$ , which is realized due to the 10 Fe  $3d$  orbitals in the up spin channel and two Fe  $3d$  orbitals in the down spin channel as shown in Fig. 2(a). Below the  $3d$  electron orbitals one would expect 12 Cl  $3p$  orbitals for each of the channel. Our calculation shows that there is prominent  $pd$  hybridization giving rise to 22 mixed orbitals in the up spin channel. The two occupied  $3d$  orbitals are found at the top of the down spin channel without any mixing with  $3p$  orbitals of Cl atoms. Interestingly, one of the  $3d$  electrons in the down spin channel is localized, and the energy difference between these two occupied  $3d$  levels is 0.84 eV. The  $3d$  electron in the highest occupied molecular orbital (HOMO) level (blue in color) is expected to be more itinerant than the other  $3d$  electrons. The itinerant electron, whose spin is opposite to both Fe ions, also satisfies the Hund's rule. In the FM state, the itinerant electron can hop from one Fe site to the other without losing the Hund's energy. This itinerant electron, which can hop from one Fe atom to other, causes a charge disproportionation between Fe atoms, namely,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , if we exclude the itinerant electron. The gain in energy due to this hopping, known as double-exchange interaction, is schematically shown in the inset of Fig. 2(a). In the case of  $\text{Fe}_2\text{Cl}_4$  cluster, the super-exchange interaction wins over this double-exchange energy gain, and the AFM state is found to be slightly (0.04 eV) lower in energy. Thus, the ground state magnetic moment depends upon a competition between the super-exchange and the double-exchange mechanism, rather than involving a direct-exchange interaction. It is important to note that the AFM state in the  $\text{Mn}_2\text{Cl}_4$  cluster is 0.18 eV (Ref. 21) lower in the energy than that of the FM state due to strong super-exchange interaction between the Mn ions.

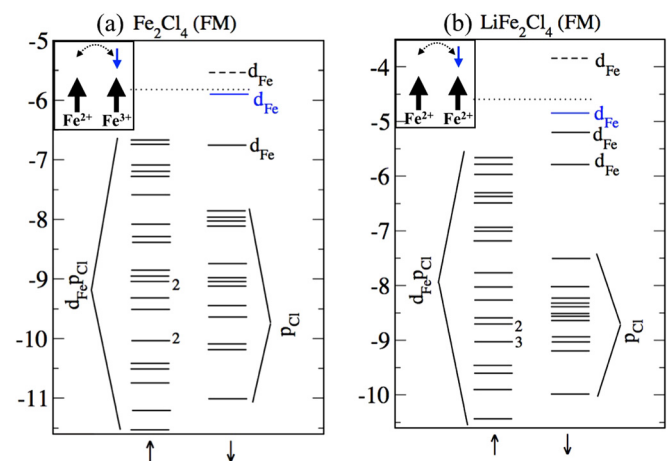


FIG. 2. One-electron energy levels (in eV) of (a)  $\text{Fe}_2\text{Cl}_4$  and (b)  $\text{LiFe}_2\text{Cl}_4$  clusters in the FM state. The solid lines represent occupied levels and the dotted lines correspond to the unfilled states. The number next to each level marks the degeneracy. Arrows at the bottom indicate the majority up and minority down spin states. The Fermi energy is shown by the dotted line. Insets show schematic diagrams of the double exchange model for the energy levels.

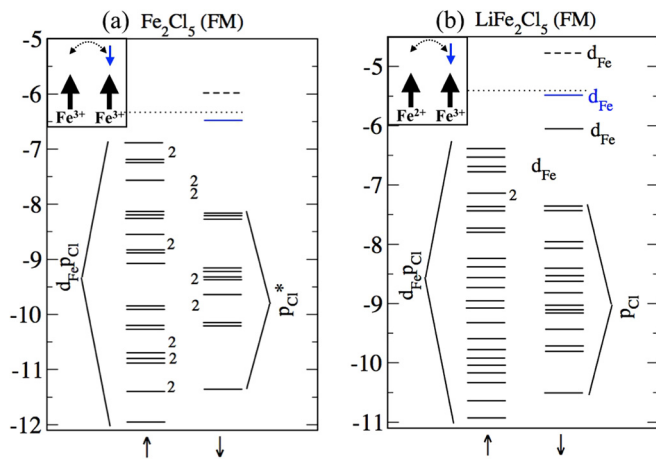


FIG. 3. One-electron energy levels of (a)  $\text{Fe}_2\text{Cl}_5$  and (b)  $\text{LiFe}_2\text{Cl}_5$  clusters in the FM state (for details, see caption of Fig. 2).

In  $\text{Fe}_2\text{Cl}_5$  cluster, there is in-built charge disproportionation ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) due to the odd number of Cl atoms attached to the Fe atoms, only if we include the down spin  $3d$  electron shown in Fig. 3(a). The  $3d$  electron in the down spin channel is itinerant and can hop between the Fe sites (both  $\text{Fe}^{2+}$  ions) in the FM configuration. There is also significant  $pd$  hybridization in the up spin channel. There are 15 electronic levels in the down spin channel which are preferably  $3p$  Cl electrons, but we find  $pd$  orbital mixing (denoted as  $p_{\text{Cl}}^*$ ) in few of these orbitals. The FM state is 0.09 eV lower than that of the AFM state. In  $\text{Fe}_2\text{Cl}_6$  cluster, both of the Fe atoms are in  $\text{Fe}^{3+}$  states, which lead to  $3d^5$  electronic states for each of the Fe ions. The AFM state is 0.2 eV lower than the FM state due to the absence of any itinerant electrons in the  $\text{Fe}_2\text{Cl}_6$  cluster.

Next, we analyze the magnetic interaction between the Fe atoms in Li doped  $\text{Fe}_2\text{Cl}_n$  clusters. It is important to see if the extra electron donated by Li atom in  $\text{LiFe}_2\text{Cl}_n$  clusters can modify the magnetic interaction between the two Fe atoms. We calculate the average charge on Cl (Fe) atoms (using Bader charge analysis<sup>30</sup>) and define  $\Delta Q_{\text{Cl}}$  ( $\Delta Q_{\text{Fe}}$ ) to measure the average charge difference between the Cl (Fe) atoms in the ground state geometry of the  $\text{LiFe}_2\text{Cl}_n$  cluster and compare it to that in the ground state geometry of the  $\text{Fe}_2\text{Cl}_n$  clusters. The charge analysis shows that Li is in +0.9 charge state and a large part of that 0.9  $e$  goes to the Cl atoms (55% in  $\text{LiFe}_2\text{Cl}_4$ , 62% in  $\text{LiFe}_2\text{Cl}_5$  and 81% in  $\text{LiFe}_2\text{Cl}_6$ ) in the  $\text{LiFe}_2\text{Cl}_n$  clusters. It is important to recall that  $\text{Cu}_2\text{Cl}_3$  is a superhalogen,<sup>23</sup> where 60% of the extra electron is distributed over the Cl atoms in the anionic  $\text{Cu}_2\text{Cl}_3$ . Next, we show that the extra electron donated by Li atom mediates the double-exchange interaction between the Fe atoms, and  $\text{LiFe}_2\text{Cl}_n$  clusters are found to be ferromagnetic.

The ground state geometries of  $\text{LiFe}_2\text{Cl}_n$  clusters are shown in Fig. 4. The two terminal atoms in  $\text{Fe}_2\text{Cl}_4$  clusters are joined together by the Li atom in the  $\text{LiFe}_2\text{Cl}_4$  clusters. As Cl atoms are successively added to the Fe atoms in  $\text{LiFe}_2\text{Cl}_5$  and  $\text{LiFe}_2\text{Cl}_6$  clusters, they assume terminal positions. The distance between the Fe atoms in  $\text{LiFe}_2\text{Cl}_n$  clusters are smaller than their respective counter part in the  $\text{Fe}_2\text{Cl}_4$  clusters.  $\text{LiFe}_2\text{Cl}_4$  cluster has a FM ground state as opposed to the AFM ground state in the  $\text{Fe}_2\text{Cl}_4$  cluster. In

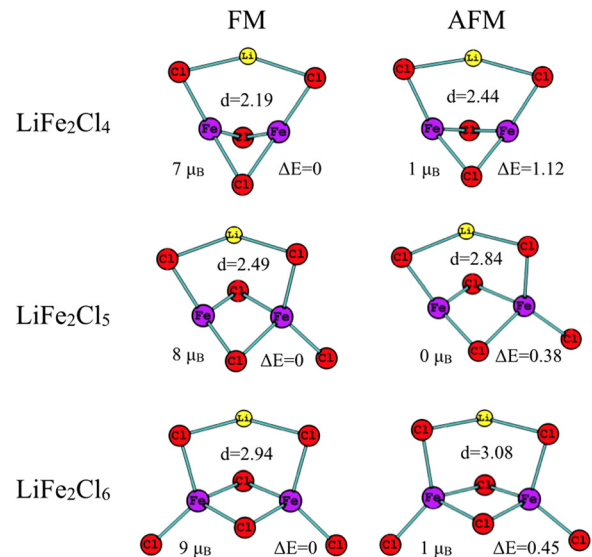


FIG. 4. Optimized ground state geometries of  $\text{LiFe}_2\text{Cl}_n$  ( $n=4-6$ ) clusters corresponding to the ferromagnetic and antiferromagnetic states. The relative energies  $\Delta E$  (in eV), magnetic moments (in  $\mu_{\text{B}}$ ) and distance ( $d$ ) between the Fe atoms (in Å) are also given.

fact, the AFM state is 1.12 eV higher in the energy than the FM state in  $\text{LiFe}_2\text{Cl}_4$ . The one-electron energy levels of the FM state of  $\text{LiFe}_2\text{Cl}_4$  cluster are shown in Fig. 2(b). The molecular orbitals are similar to that of the FM excited-state of  $\text{Fe}_2\text{Cl}_4$  cluster except the number of  $3d$  electrons in the down spin channel. The  $3d$  electron, which is close to the Fermi level, mediates the double exchange interaction between the Fe ions in the  $\text{LiFe}_2\text{Cl}_4$  cluster, which is shown schematically in the inset. The Bader charge analysis shows that 0.4  $e$  from the Li atom is transferred to the Fe atoms. At the same time, the number of  $3d$  electrons in the down spin channel increases to three for the  $\text{LiFe}_2\text{Cl}_4$  cluster. This is partly due to the decrease in the amount of  $pd$  hybridization in the energy levels of  $\text{Fe}_2\text{Cl}_4$ .

The decrease in the  $pd$  mixing in the Li doped cluster is more clear in the  $\text{LiFe}_2\text{Cl}_5$  cluster where both of the  $\text{Fe}_2\text{Cl}_5$  and  $\text{LiFe}_2\text{Cl}_5$  clusters have the FM ground state. A large part of the ionic charge (0.56  $e$ ) from the Li ion in  $\text{LiFe}_2\text{Cl}_5$  cluster goes to the Cl atoms that decreases the  $pd$  mixing in the down spin channel of the  $\text{Fe}_2\text{Cl}_5$  cluster [Fig. 3(a)]. Part of the down spin  $3d$  electrons that were mixed with  $3p$  electrons of the Cl atoms are now free in  $\text{LiFe}_2\text{Cl}_5$ , and this is why we have two  $3d$  electrons [see Fig. 3(b)]. Due to the isoelectronic configuration, the one-electron energy level of the  $\text{LiFe}_2\text{Cl}_5$  cluster looks similar to the FM configuration of  $\text{Fe}_2\text{Cl}_4$  cluster [in Fig. 2(a)] with two  $3d$  (down spin) electrons. The itinerant electron close to the Fermi level mediates the double-exchange energy, which we have explained in Fig. 2(a). Similarly, the extra  $3d$  electron in  $\text{LiFe}_2\text{Cl}_6$  cluster goes to the down spin channel and mediates the double exchange interaction between the Fe atoms. The FM states of  $\text{LiFe}_2\text{Cl}_5$  and  $\text{LiFe}_2\text{Cl}_6$  clusters are 0.38 and 0.45 eV lower in the energy than their respective AFM state. We expect  $\text{LiFe}_2\text{Cl}_7$  cluster (not studied here) to have an AFM ground state similar to that of the  $\text{LiMn}_2\text{Cl}_5$  cluster<sup>21</sup> due to the unavailability of any itinerant electrons.

TABLE I.  $\text{LiFe}_2\text{Cl}_n$  clusters:  $\Delta E$  is the relative energy of the AFM state to that of the FM state for different  $U^*$  (negative sign implies antiferromagnetic ground state).

Cluster	$\Delta E$			$\Delta E$			
	$U^* = 0 \text{ eV}$	$U^* = 1 \text{ eV}$	$U^* = 2 \text{ eV}$	$U^* = 0 \text{ eV}$	$U^* = 1 \text{ eV}$	$U^* = 2 \text{ eV}$	
$\text{Fe}_2\text{Cl}_4$	-0.04	-0.26	-0.54	$\text{LiFe}_2\text{Cl}_4$	1.12	0.81	0.46
$\text{Fe}_2\text{Cl}_5$	0.09	0.11	0.09	$\text{LiFe}_2\text{Cl}_5$	0.38	0.19	0.05
$\text{Fe}_2\text{Cl}_6$	-0.20	-0.14	-0.10	$\text{LiFe}_2\text{Cl}_6$	0.45	0.38	0.27

To incorporate the electron correlation effects, we have repeated the calculations at the DFT+U level (U is the onsite Coulomb electron-electron repulsion on the Fe atoms only). We have adopted DFT+U model proposed by Dudarev *et al.*<sup>29</sup> in which total energy depends on an effective  $U^*$  ( $=U-J$ ; U=onsite Coulomb interaction; J=exchange interaction).  $U^* = 0$  corresponds to the pure GGA limit. The energy differences between the FM states and the AFM states for  $\text{Fe}_2\text{Cl}_n$  and  $\text{LiFe}_2\text{Cl}_n$  clusters are given in Table I for moderate values of  $U^*$ . This shows that FM states are, in fact, the ground states in the  $\text{LiFe}_2\text{Cl}_n$  clusters.  $\Delta E$  in Table I decreases rapidly for  $\text{LiFe}_2\text{Cl}_5$  cluster, and the FM state and the AFM state are found to be degenerate for  $U^* = 3 \text{ eV}$ . But, we expect  $U^*$  to be smaller than the empirical value  $U^* = 3$  reported<sup>31</sup> for  $\text{Fe}_2\text{O}_3$  due to the comparatively low oxidation state of Fe atoms in the Cl ligated cluster. Further work is needed to justify the choice of  $U^*$  value in these Cl ligated Fe clusters.

In recent years, TM adatom and dimer adsorbed on 2D materials have been studied to modify the electronic and magnetic properties of 2D materials such as graphene,<sup>32</sup> BN sheet,<sup>33</sup> silicene,<sup>34</sup> and germanene,<sup>35</sup> which will be helpful in designing better devices. For example, Fe dimer adsorbed graphene is a half metal.<sup>32</sup> Most importantly, the magnetism of the TM dimers is preserved even in the presence of the host 2D materials.<sup>32,33</sup> Thus, we believe that  $\text{Fe}_2\text{Cl}_n$  and  $\text{LiFe}_2\text{Cl}_n$  clusters may retain their large magnetic moment on host 2D materials and will be very useful for technological applications. Recently, transition metals and transition metals oxides doped graphene show excellent electro-catalytic activities for fuel cell applications.<sup>36,37</sup>  $\text{Fe}_2\text{Cl}_n$  or  $\text{LiFe}_2\text{Cl}_n$  cluster could also be doped in graphene to explore their electro-catalytic activities.

In summary, our calculations based on density functional theory show that one can design molecular magnets by combining the superhalogen behavior and magnetic properties. The double-exchange and super-exchange based models explain the ground state magnetic properties of  $\text{Fe}_2\text{Cl}_n$  and  $\text{LiFe}_2\text{Cl}_n$  ( $n = 4-6$ ) clusters. The calculated energy differences between the FM and the AFM states in  $\text{LiFe}_2\text{Cl}_n$  clusters are reasonably large (see Table I) which makes these clusters promising candidates for molecular magnets. We hope that our finding will motivate further experimental works on di-nuclear transition metal based superhalogens, which will be helpful in synthesizing functional molecular magnets in the future.

This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-FG02-96ER45579.

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