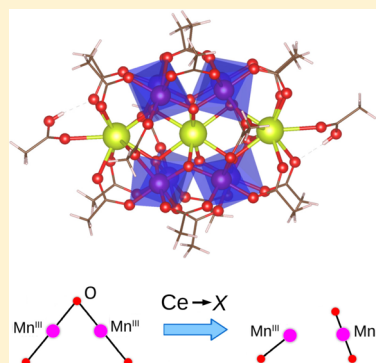


Cation Substitution Effect on a Molecular Analogue of Perovskite Manganites

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ABSTRACT: A recently synthesized Mn-containing molecule $\text{Ce}_2^{\text{III}}\text{Ce}^{\text{IV}}\text{Mn}_8^{\text{III}}\text{O}_8(\text{O}_2\text{CPh})_{18}(\text{HO}_2\text{CPh})$ ($\text{Ce}_3\text{Mn}_8^{\text{III}}$) structurally resembles the repeating unit of a bulk perovskite manganite. This resemblance brings forth the intriguing possibility of studying physical properties and effects that appear in both the molecule and the far more complex bulk perovskites, for example, effects of cation substitution, which in bulk manganites may lead to phase transition from metallic-ferromagnetic to insulating-paramagnetic as well as the colossal magnetoresistance effect. We investigate divalent and trivalent cation substitution in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecules and its effects on ground-state magnetic configuration using first-principles-based approaches. One Mn^{III} ion changes its valence to Mn^{IV} after trivalent (including La, Gd) cation substitution, while four Mn^{III} ions become Mn^{IV} upon divalent (including Ca, Sr, Ba, and Pb) cation substitutions, all accompanied by vanishing local Jahn–Teller distortion around Mn^{IV} . The valence state of Mn^{IV} induced by cation substitutions can hop among Mn sites in molecule, and the calculated energy barrier for such state hopping is 0.25 to 0.6 eV/molecule. In addition, the charging energies of the $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule and its derivatives are found to be strongly dependent on the spin direction of added electron.



I. INTRODUCTION

Perovskite manganites continue to gain interest owing to the fascinating physical properties such as colossal magnetoresistance and multiferroicity.^{1–6} A molecular bottom-up approach to make a fragment of these 3D solids can overcome the limitations and complexities encountered in the synthesis and characterization of bulk 3D materials. Molecules with a stabilizing shell of organic ligands possess important advantages over 3D solids. These advantages of molecules are well illustrated in the field of single-molecule magnets (SMMs)^{7,8} for discovering new physical phenomena. In a previous work, we synthesized and studied the $[\text{Ce}_2^{\text{III}}\text{Ce}^{\text{IV}}\text{Mn}_8^{\text{III}}\text{O}_8(\text{O}_2\text{CPh})_{18}(\text{HO}_2\text{CPh})]$ ($\text{Ce}_3\text{Mn}_8^{\text{III}}$) molecule, which is the first example of a molecular analogue of the perovskite manganite repeating units.⁹ The structure of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule is shown in Figure 1. The eight MnO_6 octahedra in the molecule reside at the sites of a slightly distorted tetragonal lattice and three Ce ions are located between MnO_6 octahedra. The structure of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule resembles the perovskite manganites but is distinct from other transition-metal-containing magnetic molecules. The central Ce ion has a valence of +4 and the other two have a valence of +3, which makes the molecule as one of the few 3d–4f complexes exhibiting mixed-valent lanthanides.^{10,11} The synthesis of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule paves the way for a bottom-up molecular approach to gaining insights into physical properties of ultrasmall perovskite nanoparticles. This molecule also provides a unique opportunity to study the effect of Ce-f orbitals on the magnetic properties. We identified that Ce^{IV}-f orbital

participates in the direct Mn–Ce–Mn magnetic coupling pathway in our previous work. The study of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule may shed light on further synthesis and study of CeMnO_3 and other rare-earth-containing materials.

In this work we further investigated the cation substitution effect in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule. All of the Mn cations in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ exhibit a valence state of +3, which is the same as in RMnO_3 (R: trivalent rare earth elements), the parent phase of doped perovskite manganites. It is well established that doped RMnO_3 can exhibit phase transitions from metallic-ferromagnetic to insulating-antiferromagnetic upon cation substitutions,^{12,13} and the colossal magnetoresistance emerges at the proper doping concentration.^{14,15} Cation substitution effect in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule is different from perovskite manganites due to the nanoscale size of the molecule. While ligand replacement was used for improving the magnetic properties of single molecular magnets,^{16,17} we demonstrated in this work that cation substitution is an alternative approach for tuning the physical properties of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule. In this work we considered the substitution by divalent cations including Ca, Sr, Ba, and Pb and by trivalent cations including La and Gd. Besides cation substitutions, cation or anion vacancy is an important factor for determining the electronic properties of bulk perovskite

Special Issue: ISSPIC XVIII: International Symposium on Small Particles and Inorganic Clusters 2016

Received: November 30, 2016

Revised: January 13, 2017

Published: January 17, 2017



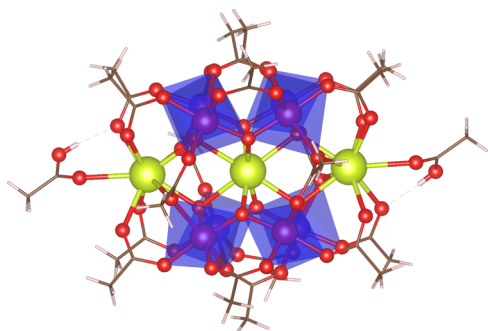


Figure 1. Atomic structure of $\text{Ce}_2^{\text{III}}\text{Ce}^{\text{IV}}\text{Mn}_8^{\text{III}}\text{O}_8(\text{O}_2\text{CPh})_{18}(\text{HO}_2\text{CPh})$ ($\text{Ce}_3\text{Mn}_8^{\text{III}}$) molecule. The MnO_6 octahedra are shaded in purple. Red: oxygen, green: cerium, brown: carbon, white: hydrogen. Figures are prepared using the VESTA software.

crystals.^{18,19} Vacancies will introduce severe disturbances to the structure of nanoscale clusters and deteriorate their stability. The perovskite core of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule consists of 8 Mn cations and 8 O anions. If one creates a cation or an anion vacancy, then the concentration of vacancy is 0.12, which is about two times of the highest vacancy concentration in bulk perovskite materials.¹⁸ We did not consider the vacancy effect in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule in this work.

$\text{Ce}_3\text{Mn}_8^{\text{III}}$ and other magnetic molecules can also be used as magnetic quantum dots. For quantum dots weakly coupled to electrodes, their self-capacitance is related to the energy for charging and discharging of the system and hence the quantum-transport properties in the Coulomb blockade regime. The self-capacitance of quantum dots is meaningful only through the quantum definition because of their discrete energy levels. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) play critical roles. The self-capacitance is determined by the single-electron charging energy, E_c , where the latter is derived to be the difference between the ionization potential (IP) and the electron affinity (EA)²⁰

$$E_c = \frac{e^2}{C(N)} = \text{IP}(N) - \text{EA}(N) \quad (1)$$

The IP is defined as the total energy difference between systems with N and $N - 1$ electrons (N is the number of electrons in the charge neutral state), $\text{IP}(N) = E_{\text{tot}}(N - 1) - E_{\text{tot}}(N)$, while EA is defined as $\text{EA}(N) = E_{\text{tot}}(N) - E_{\text{tot}}(N + 1)$. Note that both IP and EA can be spin-dependent in magnetic quantum dots. The coupling of molecular orbitals near the energy gap (especially the LUMO and HOMO) to the spin order and molecular conformation provides routes to control the spin-dependent self-capacitance of molecules.

In a previous work we predicted that some magnetic molecules exhibit distinct self-capacitance in the high-spin and low-spin states.²¹ We also found that charging can drive conformational changes to nanoclusters, which leads to a hysteresis in the current–voltage curve in the Coulomb region;²² the same phenomena was observed in experiments.²³ In this study we calculated the self-capacitance of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ and its derivatives.

The rest of the paper is organized as follows: Section II describes the first-principles-based method used in this study. The results of our calculations are presented in Section III, which is divided into two subsections. In Subsection III.A, we

discuss the effect of cation substitution on the molecular structure, magnetic state, and the valence state hopping in $\text{Mn}_8^{\text{III}}\text{Ce}_3$ derivatives. The charging energies, in particular, their dependence on the spin direction of the injected electron, are reported in Subsection III.B. A summary is given in Section IV.

II. COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were carried out using the VASP code.^{24,25} The projector augmented wave potentials²⁶ were employed to describe the electron–ion interaction. Wave functions were expanded using a plane-wave basis set with an energy cutoff of 500 eV. We used the Perdew–Burke–Ernzerhof (PBE) parametrization²⁷ of the generalized gradient approximation (GGA) of the exchange–correlation functional, which is capable of reproducing the magnetic interactions in $\text{Ce}_3\text{Mn}_8^{\text{III}}$. The molecule was put in a large periodic supercell of $28 \text{ \AA} \times 22 \text{ \AA} \times 24 \text{ \AA}$. The distance between a molecule and its periodic images is $>10 \text{ \AA}$, so the negligible van der Waals interaction among them was not considered in the calculation. Electric monopole and dipole corrections were employed for charged systems to ensure total energy convergence. The atomic structure of unsubstituted molecules was optimized using the damped molecular dynamics approach until the residual force on each atom was $<0.01 \text{ eV/\AA}$. We used the climbing image nudged elastic band method^{28,29} (CI-NEB) implemented in the Transition State Tools for VASP (VTST)³⁰ to identify the pathway between different charge-ordering configurations.

III. RESULTS AND DISCUSSION

III.A. Valence State Hopping. The $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule and its derivatives bear a striking structural resemblance to the repeating unit of perovskite manganites. The three Ce ions in the unsubstituted $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule (Figure 1) reside on a line, denoted as the Ce line hereafter, which can be used as a reference for describing the molecular structure. The eight Mn^{III} ions in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule can be divided into two groups; each group consists of four Mn ions, which are structurally separated by the Ce line: MnO_6 octahedra in the top and bottom groups share neither corners nor edges across the Ce line. Within each Mn group, MnO_6 octahedra share one corner, that is, one bridging oxygen along the direction normal to the Ce line, while along the direction of the Ce line they share an edge, that is, two bridging oxygen atoms.

Substitution of Ce ions by tri- and divalent cations induces changes in the valence state of Mn ions. In unsubstituted $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule, Ce ions serve as electron donors and contribute 10 electrons in total: each of two Ce ions at the ends of the Ce chain contributes three electrons, while the central one contributes four. Substitution of Ce ions by tri- and divalent ions reduces the number of electrons contributed by these cations. As a result, some of the Mn^{III} ions in the unsubstituted compound become Mn^{IV} . Substitution of all Ce ions by trivalent cations turns one Mn^{III} ion to Mn^{IV} , while divalent substitution turns four Mn^{III} ions to Mn^{IV} . We identified the changes in the valence states of Mn ions through examining their local magnetic moments. The calculated atom-projected magnetic moment is $\sim 3.5 \mu_B$ for each Mn^{III} ion but only $\sim 2.6 \mu_B$ for each Mn^{IV} ion.

Substitution of Ce ions by tri- and divalent cations induces structural changes as a result of the changes in the valence state of Mn ions. Oxygen octahedra surrounding Mn^{III} ions exhibit

strong Jahn–Teller distortions with two elongated Mn–O bonds as long as 2.2 Å compared with 1.9 Å of the other four, while no such distortion occurs for Mn^{IV}O₆ octahedra. Figure

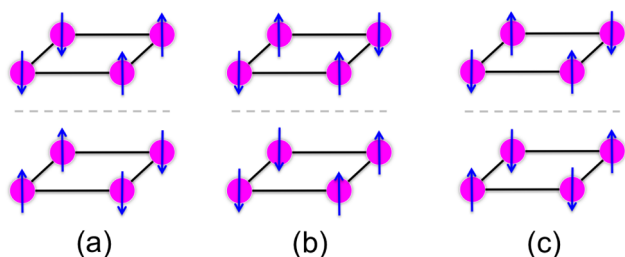


Figure 2. Spin configurations of (a) unsubstituted Ce₃Mn₈^{III}, (b) Mn₈Rn₃ with Rn = La, Gd, and (c) Mn₈Ae₃ with Ae = Ca, Sr, Ba, Pb. The dashed lines denote the Ce lines. All of the Mn's in panel a have a valence state of Mn^{III}. One of the Mn's above the Ce line in panel b becomes Mn^{IV}. Two of the Mn's along the diagonal direction above the Ce line and two of the Mn's along the other diagonal direction below the Ce line become Mn^{IV} in panel c.

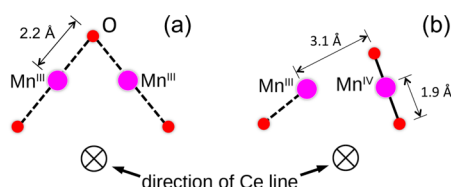


Figure 3. (a) Schematics of the local atomic structure in unsubstituted Ce₃Mn₈^{III} molecule, in which the chemical bond to the bridging oxygen is 2.2 Å, longer than the other Mn–O bonds not shown in the Figure. (b) One of the Mn ion becomes Mn^{IV} after cation substitutions. The bridging oxygen is taken by the Mn^{IV} ion, while the distance to the Mn^{III} becomes as long as 3.1 Å. The Ce line direction is perpendicular to the plane of paper.

3a schematically shows how the two Mn^{III}O₆ octahedra in unsubstituted Ce₃Mn₈^{III} share one bridging oxygen along the direction of the Ce line. The Mn–O bond connecting Mn^{III} ions to the bridging oxygen and the Mn–O bond in the opposite direction are the two elongated Mn–O bonds with bond length of 2.2 Å. The other four Mn–O bonds of 1.9 Å are not shown in Figure 3a. Upon cation substitutions one of the Mn^{III} becomes Mn^{IV}, as illustrated in Figure 3b. All Mn^{IV}–O bonds are as short as 1.9 Å, which leads to bond breaking between the bridging oxygen and the Mn^{III} ion, leaving a distance between the two longer than 3 Å.

The spin configuration in the ground state is also changed by cation substitution. The ground state of Ce₃Mn₈^{III} has a C-type antiferromagnetic configuration (Figure 2a). Upon divalent cation substitution two Mn's on the diagonal direction on the top Mn₄ group and two Mn's on the other diagonal direction on the bottom Mn₄ group become Mn^{IV}. The spin configuration becomes G-type (Figure 2c), in which all nearest-neighbor Mn pairs have their magnetic moments antiparallel to each other. The trivalent cation substituted compounds shown in Figure 2b have a spin configuration between C-type and G-type. One Mn ion of the top Mn₄ group becomes Mn^{IV}, and the local magnetic moments of Mn ions are antiparallel in both the directions normal to and along the Ce line. Mn ions in the bottom Mn₄ group keep the same spin configuration as in unsubstituted Ce₃Mn₈^{III}.

Besides spin order, cation substitutions also change the charge order of Ce₃Mn₈^{III} molecule. The charge orders refer to the distribution of Mn^{IV} ions within the molecule. For trivalent substitutions, there is only one Mn^{IV} ion introduced by substitution, and the Mn^{IV} ion can reside in any of the eight Mn sites. As for divalent substitutions, two of the Mn^{IV} ions reside on the top Mn₄ group, while the other two reside on the bottom Mn₄ group.

The system can transform from one charge-ordering configuration to another. One or more Mn^{III} exchanges its valence state with its Mn^{IV} neighbors. This process does not involve long distance movement of Mn ions but instead involves the collective motion of several atoms.

We only consider the valence-state exchange within the top or the bottom Mn₄ group. For the trivalent cation-substituted Ce₃Mn₈^{III}, the valence state of Mn^{IV} can go from one Mn site to any of the other three on the same Mn₄ group. We calculated the valence-state exchange pathway using the CI-NEB method. The pathway was sampled using nine images, as shown in Figure 4. The first image corresponds to the structure with the

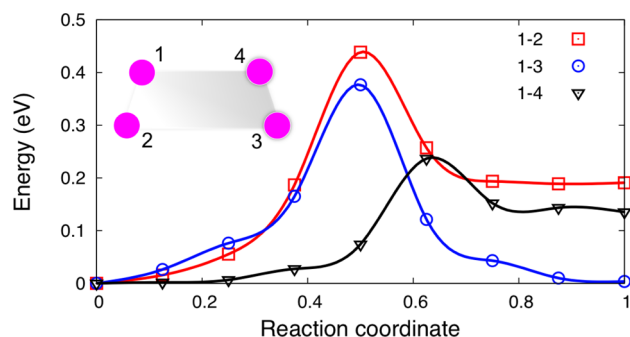


Figure 4. Energy landscape of the transitions between different charge ordering configurations of the La-substituted Ce₃Mn₈^{III} molecule. The charge ordering configuration is characterized by the position of the Mn^{IV} ion.

Mn^{IV} ion residing on site denoted as 1 (see inset of Figure 4), and the last image corresponds to Mn^{IV} ion on sites 2, 3, and 4, respectively. We assigned a reaction coordinate to each image. The first and last images have reaction coordinates of 0 and 1, respectively, and the reaction coordinates of the remaining images are distributed evenly between 0 and 1. The energy landscape along the pathway gives the energy barrier for the valence state exchange process. The calculated height of energy barrier is between 0.2 and 0.5 eV, as shown in Figure 4.

For the case of divalent cation substitution, the energy landscape for valence state exchange is more complex; see Figure 5a. An energy barrier of 0.6 eV needs to be overcome during this process. The process of valence state exchange is schematically shown in Figure 5b–d, where Mn^{IV} is characterized as covalently bonded to an oxygen (small red disk in Figure 5). The valence state exchange process can be divided into two steps. The energy landscape of each step was calculated using the CI-NEB method with six images. Reaction coordinates were assigned to images in the same manner as Figure 4. For each step the valence state exchange occurs between a pair of Mn's; the structural change during this process is primarily from the large displacement of the bridging oxygen, as shown in Figure 5.

Next, we compare the substituted Ce₃Mn₈^{III} molecules with the perovskite manganite La^{III}Mn^{III}O₃. Pure La^{III}Mn^{III}O₃ is an

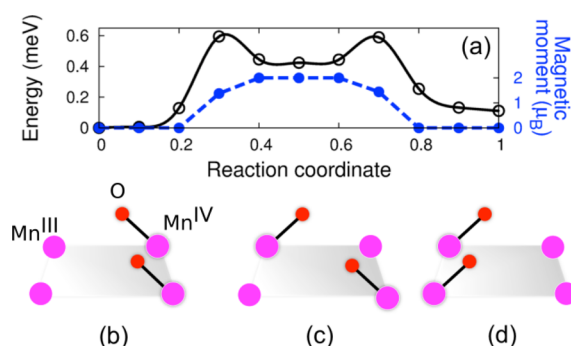


Figure 5. Process and energy landscape of valence state hopping in the Ba-substituted $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule. The energy landscape and the magnetic moments of each state along the reaction coordinate are shown in panel a. Panels b–d are schematics of the structures with reaction coordinates 0.0, 0.5, and 1.0, respectively. In panels b–d, Mn^{IV} ions are bonded to oxygen atoms (red dots), while Mn^{III} ions are not linked.

antiferromagnetic insulator. Substitutions of La^{III} ions in $\text{La}^{\text{III}}\text{Mn}^{\text{III}}\text{O}_3$ by divalent ions (e.g., Sr) turn Mn^{III} ions to Mn^{IV} , just as in substituted $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecules. With an optimal percentage of La^{III} ions substituted, doped $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ becomes a ferromagnetic metal, which can be explained using the double-exchange theory proposed by Zener.^{31–34} Although the spin order in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule can be modified by cation substitutions, no ferromagnetic order emerges.

III.B. Charging Energies. Hund's rule asserts the high spin state as the atomic ground state of Mn^{III} and Mn^{IV} ions. Suppose that there is a Mn^{IV} ion with local magnetic moment along the spin-up direction. An injected electron with an up spin will have a lower energy and become localized around this Mn ion. If the injected electron has a down spin, then it cannot fit in this Mn ion and may become delocalized within the molecule if it fails to find another Mn ion with down spin. Furthermore, if the molecular structure is allowed to relax in the presence of the injected electron, then the injected electron with up spin will induce Jahn–Teller distortions around the Mn^{IV} ion and push it to the Mn^{III} valence state. We thus expect that the charging energy depends on the spin direction of the injected electron, without and with structural relaxations.

Here we consider the added electron can have its spin in the up or down direction, that is, spin dependence of the anion state. We computed charging energies of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ and its derivatives using three different atomic structures. The

structure optimized at the charge neutral state is denoted as the neutral structure; the calculated charging energies using this structure are denoted as $E_c^{\text{N}\uparrow}$ and $E_c^{\text{N}\downarrow}$ when the injected electron in the anion state is at spin-up and spin-down states, respectively. Structures relaxed at the anion state with the injected electron fixed in the spin-up and spin-down state are denoted as $\text{Anion}^{\uparrow}$ and $\text{Anion}^{\downarrow}$ structures; the calculated charging energies using these two structures are referred to as $E_c^{\text{A}\uparrow}$ and $E_c^{\text{A}\downarrow}$. Calculated charging energies using the neutral structure ($E_c^{\text{N}\uparrow}$ and $E_c^{\text{N}\downarrow}$ in Table 1) are larger than those using anion structures ($E_c^{\text{A}\uparrow}$ and $E_c^{\text{A}\downarrow}$) by 0.5 to 1.2 eV. According to Table 1 the difference in charging energies is dominated by the difference in the EA term. In schemes II and III we performed structural relaxation of the $(N + 1)$ -electrons system, resulting in a higher $E_{\text{tot}}(N)$ and a lower $E_{\text{tot}}(N + 1)$ than those calculated using the neutral structure.

The spin-dependent charging energy difference using the neutral structure (ΔE_c^{N} in Table 1) is ~ 0.1 eV for unsubstituted $\text{Mn}_8^{\text{III}}\text{Ce}_3$ and the trivalent substituted derivatives (Mn_8La_3 and Mn_8Gd_3); the differences are enhanced up to 0.3 to 0.4 eV when using the anion structures (ΔE_c^{A}). The spin dependence of charging energy in divalent cation substituted derivatives (Mn_8Ca_3 , Mn_8Sr_3 , Mn_8Ba_3 , and Mn_8Pb_3) is very weak for both neutral and anion structures. The enhancement of ΔE_c^{A} over ΔE_c^{N} can be traced back to the difference in the $\text{Anion}^{\uparrow}$ and $\text{Anion}^{\downarrow}$ structures. Using the neutral structure as a reference, the $\text{Anion}^{\uparrow}$ structures of La_3Mn_8 and Gd_3Mn_8 show a significant relaxation near the Mn^{IV} ion, where two of the Mn–O bonds elongated up to 2.2 Å, which is the Jahn–Teller distortion seen around a Mn^{III} ion. The injected electron with up spin drives the spin-up Mn^{IV} ion to the Mn^{III} state. In contrast, the $\text{Anion}^{\downarrow}$ structure shows no clear derivation from the neutral structure. Divalent cation-substituted variations contain both spin-up and spin-down Mn^{IV} ions. The injected electron can always find a Mn^{IV} ion with the same spin direction. Both the $\text{Anion}^{\uparrow}$ and $\text{Anion}^{\downarrow}$ structures show Jahn–Teller distortions, although on different Mn^{IV} sites. As a result the spin-related charging energy difference of Mn_8Ca_3 , Mn_8Sr_3 , Mn_8Ba_3 , and Mn_8Pb_3 remains small, even with structural relaxations.

Not only are the HOMO and LUMO critical to the charging energy of molecules, but also their shapes can reveal the underlying structural relaxation. The corresponding charge density of the LUMO wave function of the neutral structure and those of the HOMO wave functions of the anion state in the anion structures are plotted in Figure 6.

Table 1. Calculated Ionization Potential IP, EA, and Charging Energies (all in eV per molecule) of the $\text{Ce}_3\text{Mn}_8^{\text{III}}$ Molecule and Its Cation-Substituted Derivatives^a

	neutral structure						ΔE_c^{N}	anion [↑] structure			anion [↓] structure			ΔE_c^{A}
	IP	EA	$E_c^{\text{N}\uparrow}$	IP	EA	$E_c^{\text{N}\downarrow}$		IP	EA	$E_c^{\text{A}\uparrow}$	IP	EA	$E_c^{\text{A}\downarrow}$	
Mn_8Ce_3	5.799	2.529	3.270	5.799	2.650	3.149	0.121	5.974	3.177	2.797	6.012	3.502	2.509	0.288
Mn_8La_3	5.869	2.225	3.644	5.869	2.236	3.513	0.131	6.101	3.374	2.627	5.925	2.924	3.001	0.374
Mn_8Gd_3	5.858	2.218	3.640	5.858	2.339	3.519	0.121	5.925	2.931	2.994	6.102	3.487	2.615	0.379
Mn_8Ca_3	6.347	2.380	3.967	6.347	2.420	3.927	0.040	6.472	3.663	2.809	6.556	3.761	2.795	0.014
Mn_8Sr_3	6.357	2.340	4.016	6.357	2.401	3.956	0.060	6.437	3.646	2.791	6.479	3.747	2.732	0.059
Mn_8Ba_3	6.320	2.373	3.947	6.320	2.454	3.866	0.081	6.425	3.685	2.740	6.474	3.789	2.685	0.055
Mn_8Pb_3	6.342	2.449	3.893	6.342	2.475	3.866	0.027	6.466	3.700	2.766	6.518	3.824	2.694	0.072

^a $E_c^{\text{N}\uparrow}$ and $E_c^{\text{N}\downarrow}$ are the spin-up and spin-down charging energies for the neutral structure; boldface ΔE_c^{N} denotes their difference. $E_c^{\text{A}\uparrow}$ and $E_c^{\text{A}\downarrow}$ correspond to charging energies calculated using the $\text{Anion}^{\uparrow}$ and the $\text{Anion}^{\downarrow}$ structures; boldface ΔE_c^{A} denotes their difference.

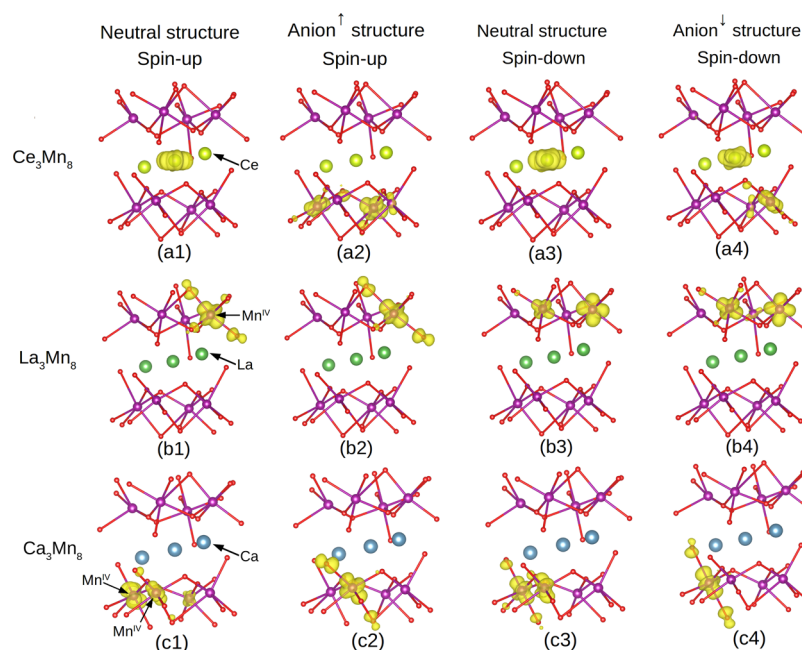


Figure 6. Isosurfaces of charge density of (a) spin-up anion state HOMO with neutral geometry, (b) spin-down anion state HOMO with neutral geometry, (c) spin-up anion state HOMO with relaxed geometry after spin-up electron charging, and (d) spin-up anion state HOMO with relaxed geometry after spin-up electron charging in Mn_8La_3 molecule.

The $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule (Figure 6a1–a4) in the neutral structure has its LUMO localized on the central Ce ion for both spin-up (a1) and spin-down (a3) channels. After structural relaxation, the HOMO at the spin-up channel with the Anion[↑] structure totally shifts to the bottom Mn_4 group (a2), while the HOMO in the spin-down channel only partially shifts (a4). The different shapes of HOMO reflect the difference between Anion[↑] and Anion[↓] structures, in accordance with the big spin-related charging energy difference.

The spin-up LUMO of La_3Mn_8 molecule (Figure 6b1–b4) with the neutral structure is localized at the Mn^{IV} ion and has a d_{z^2} -like shape (b1), while the spin-down LUMO is a superposition of the d_{xy} orbital on the Mn^{IV} ion and the $d_{x^2-y^2}$ orbital on neighboring Mn^{III} ion (b3). The spin-up LUMO in the Anion[↑] structure (b2) preserves the same d_{z^2} -like shape as in (b1) but has a more localized spatial distribution. The spin-down LUMO in the Anion[↓] structure (b4) spread out onto another neighboring Mn^{III} ion and is more delocalized with respect to (b3). The Anion[↑] structure makes its HOMO more spatially localized; in contrast, the HOMO of Anion[↓] structure becomes more delocalized.

The HOMO and LUMO orbitals of two spin channels are much more symmetric in divalent cation-substituted Ca_3Mn_8 (Figure 6c1–c4) than Ce_3Mn_8 and La_3Mn_8 , which agrees with the small spin-related charging energy differences (ΔE_c^{N} and ΔE_c^{A} in Table 1). The LUMOs of the neutral structure for both the spin-up and spin-down channels are superpositions of d_{z^2} orbital on the Mn^{IV} ion with the same spin and the d_{xy} orbital on the neighboring Mn^{IV} ion with antiparallel spin. After relaxations, the HOMO becomes strongly localized to the d_{z^2} orbital (c2 and c4).

IV. SUMMARY

We investigated the perovskite-analog $\text{Ce}_3\text{Mn}_8^{\text{III}}$ molecule and its derivatives via divalent and trivalent cation substitutions. The behavior of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ derivatives upon cation substitutions

is similar to perovskite manganites in some aspects. Cation substitutions change the valence state of Mn ions, and the molecular structure, in particular, the Jahn–Teller distortion and the magnetic ground states, but unlike doped perovskite manganites (such as $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$), the ferromagnetic ground state in $\text{Ce}_3\text{Mn}_8^{\text{III}}$ derivatives is not accessible by cation substitutions. The valence state hopping needs to overcome an energy barrier of 0.2 to 0.5 eV. We also studied the self-capacitance properties of these molecules. We found that the charging energies of $\text{Ce}_3\text{Mn}_8^{\text{III}}$ and trivalent cation-substituted derivatives strongly depend on the spin direction of the injected electron, while the spin dependence in divalent cation-substituted derivatives is weak; the spin dependence is analyzed via the spatial distributions of the HOMO and LUMO orbitals in the two spin channels.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the U.S. National Science Foundation DMREF program under Grant No. 1534401. Calculations were performed at the National Energy Research Scientific Computing Center and at UF Research Computing.

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