Density Functional Theory Study on Electronic and Magnetic Properties of Mn-doped (MgO)$_n$ ($n=2$–$10$) Clusters


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We study the geometries, stabilities, electronic and magnetic properties of (MgO)$_n$ ($n=2$–$10$) clusters doped with a single Mn atom using the density functional theory with the generalized gradient approximation. The optimized geometries show that the impurity Mn atom prefers to replace the Mg atom which has low coordination number in all the lowest-energy MnMg$_{n-1}$O$_n$ ($n=2$–$10$) structures. The stability analysis clearly represents that the average binding energies of the doped clusters are larger than those of the corresponding pure (MgO)$_n$ clusters. Maximum peaks of the second order energy differences are observed for MnMg$_{n-1}$O$_n$ clusters at $n=6$, 9, implying that these clusters exhibit higher stability than their neighboring clusters. In addition, all the Mn-doped Mg clusters exhibit high total magnetic moments with the exception of MnMgO$_2$ which has 3.00 $\mu_B$. Their magnetic behavior is attributed to the impurity Mn atom, the charge transfer modes, and the size of MnMg$_{n-1}$O$_n$ clusters.

Key words: Density functional theory, MnMg$_{n-1}$O$_n$ cluster, Electronic property, Magnetic property

I. INTRODUCTION

Recently, much attention has been paid to MgO nanostructures, which exhibit diverse applications in catalysis, refractory, paint, and superconductor material industries [1–8]. Likewise, a large number of experimental and theoretical researches have been done on MgO clusters. Experimentally, Saunders et al. reported mass-spectra and collision-induced-fragmentation data for sputtered MgO cluster ions [9, 10]. They found that the most abundant clusters for (MgO)$_n$ ($n=2, 4, 6, 9, 12, 15, 18, 24, 27,$ and 30) [11, 12]. Haertelt et al. studied (MgO)$_n$ ($n=90$) clusters by using laser-ionization time of flight mass spectrometry, and pointed out that magic number clusters for (MgO)$_n$ were those with cluster sizes of $n=6, 9, 12, 15, 18, 24, 27,$ and 30 [11, 12]. Ziemann et al. studied (MgO)$_n$ ($n=90$) clusters by using laser-ionization time of flight mass spectrometry, and pointed out that magic number clusters for (MgO)$_n$ were those with cluster sizes of $n=6, 9, 12, 15, 18, 24, 27,$ and 30 [11, 12]. Haertelt et al. obtained structural information for neutral MgO clusters by a comparison of their experimental vibrational spectra with predictions from theory [13]. Theoretically, many first principles studies have been done for small (MgO)$_n$ clusters ($n \leq 15$) [14–19]. Moreover, the strong shape dependence of electronic properties in small magnesium clusters has been reported by Moukouri and Noguera [20, 21] with a tight binding calculation. Robert et al. predicted (MgO)$_n$ clusters by using genetic algorithm and found that hexagonal stacks were stable for small (MgO)$_n$ clusters [22]. Jain et al. studied various (MgO)$_n$ ($1 \leq n \leq 13$) isomers for each cluster size to find the lowest energy structures and to identify the magic clusters using first principles calculations [23]. Their results confirmed that clusters with $n=4, 6, 9,$ and 12 are magic in agreement with the available experimental data. Using density functional theory (DFT), Dong et al. investigated the structures and stabilities of (MgO)$_{3n}$ ($2 \leq n \leq 10$) clusters [24]. It was found that the hexagonal-tube structure was the most stable one in the range of $n=2$–$5$, and the rocksalt-like structure was favored starting from $n=6$. Using a hybrid $ab$ initio genetic algorithm method, Kwapien et al. recently investigated the structural diversity and flexibility of MgO gas-phase clusters [25]. Zhang et al. investigated the melting behavior and thermal stability of (MgO)$_n$ ($n=18, 21,$ and 24) clusters by molecular dynamics simulations [26].

Up to now, there are very few evidences of introducing magnetism into (MgO)$_n$ clusters. Recently, the magnetism of the pure metal clusters with multiple metal centres [27, 28] and doped atomic oxide clusters has been exploited by many research groups, such as the magnetic behavior of TiO$_2$, SnO$_2$, In$_2$O$_3$, HfO$_2$, and the more popular ZnO [29–33]. Pure magnesia clusters in nature has no magnetism. Therefore, it would be in-

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teresting to know how the properties of small \((\text{MgO})_n\) clusters change after introducing a single Mn impurity atom. To investigate this question, we have performed a systematic study on geometries, stabilities, electronic structures, and the magnetism of these Mn-doped magnesia clusters using DFT calculations.

II. COMPUTATIONAL METHODS

All the calculations are performed with the DMol\(^3\) package [34]. The exchange-correlation interaction is treated within the generalized-gradient approximation (GGA) using Perdew, Burke, and Ernzerhof (PBE) functional [35]. There are no symmetry constraints for the optimization of pure and Mn-doped \((\text{MgO})_n\) \((n=2-10)\) structures. All-electron relativistic calculations are used for pure magnesia clusters, which are time-consuming for Mn atom. Thus, the DFT-based semi-core pseudopotentials treatment is chosen for all the Mn-doped magnesia clusters. Double numerical basis sets including polarization functions on all atoms (DNP) are performed [36, 37]. The convergence criteria applied during geometry optimization are set to \(10^{-5}\) Hartree for energy. In order to accelerate SCF convergence, we use Pulay’s direct inversion of iterative subspace (DIIS) technique. The global cutoff radius of Mn-doped clusters is set to be 4.9 Å, and smearing is 0.005 Hartree. The different possible spin multiplicities are considered for each Mn-doped configuration to ensure that the obtained spin states are the most favorable in energy [38]. A I point of \(1 \times 1 \times 1\) has been taken into account when we calculate the spin-resolved electronic density of states of the Mn-doped magnesia clusters. In the structural optimization, vibrational frequency calculations are carried out to verify that all the structures correspond to true minima in the potential energy surface.

III. RESULTS AND DISCUSSION

A. Geometries of \(\text{MnMg}_{n-1}\text{O}_n\) \((n=2-10)\) clusters

Considering a series of possible initial configurations, we have calculated the pure \((\text{MgO})_n\) \((n=2-10)\) clusters by using DFT calculations. The chosen \((\text{MgO})_n\) structures are in their global minimum, which has been investigated using genetic algorithm simulation based on Born-Mayer potential [25]. The lowest-energy optimized structures are presented in Fig. 1, which are in good agreement with the previous theoretical research [24, 39]. The doping structures are obtained by replacing one magnesium atom with a manganese atom in all the possible positions of the lowest-energy \((\text{MgO})_n\) clusters \((n=2-10)\). The optimized Mn-doped \((\text{MgO})_n\) clusters are also shown in Fig. 1. It should be mentioned that the obtained Mn-doped \((\text{MgO})_n\) clusters are not exactly the most stable by the method. The symmetry, spin multiplicity, relative energy \((\Delta E)\) with respect to the lowest-energy structure, HOMO-LUMO gaps, and total magnetic moment for Mn-doped magnesia clusters are summarized in Table I. For the sake of simplicity, the Mn-doped \((\text{MgO})_n\) is designated as \(\text{MnMg}_{n-1}\text{O}_n\), where \(n\) is the symbol of cluster size \((n=2-10)\). The isomers of \(\text{MnMg}_{n-1}\text{O}_n\) clusters are named by \(a, b, c, d, e\) and so on.

As displayed in Fig. 1, only one independent Mn-doped structure is found for the clusters with \(n=2, 3, 4, 6,\) and 8. Our calculations show that the ground quartet state of \(\text{MnMg}_2\text{O}_3\) is a four-membered ring with \(C_2\) symmetry corresponding to \(\mu=3.00\) \(\mu_B\). The non-planar and ring type \(\text{MnMg}_2\text{O}_3\) cluster is in a sextet state with 4.98 \(\mu_B\). In the \(\text{MnMg}_2\text{O}_3\), the cubic structure with rhombohedral distortion is found. The cubic \(\text{MnMg}_2\text{O}_4\) has low symmetry \((C_1)\), while the corresponding pure cluster \((\text{MgO})_4\) has a high symmetry of \(T_d\). In the case of \(\text{MnMg}_3\text{O}_5\), \(5a\) with \(C_5\) symmetry is the most energetically preferred one. It is gained by substituting the Mg atom which has coordination number two in \((\text{MgO})_5\) with an Mn atom. Other isomers of \(\text{MnMg}_4\text{O}_5\) clusters including \(5b, 5c, 5d,\) and \(5e\) with low symmetry are less stable than that of \(5a\) by 0.569–0.692 eV in energy as shown in Table I. For \(\text{MnMg}_5\text{O}_6\), the most stable structure is stacking of two

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Symm.</th>
<th>(M)</th>
<th>(\Delta E/eV)</th>
<th>(E_g/eV)</th>
<th>(\mu/\mu_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{MnMg}_2\text{O}_3)</td>
<td>2v</td>
<td>Sextet</td>
<td>0.000</td>
<td>0.707</td>
<td>3.00</td>
</tr>
<tr>
<td>(\text{MnMg}_3\text{O}_4)</td>
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<td>0.000</td>
<td>1.271</td>
<td>4.98</td>
</tr>
<tr>
<td>(\text{MnMg}_4\text{O}_5)</td>
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<td>Sextet</td>
<td>0.000</td>
<td>0.920</td>
<td>5.00</td>
</tr>
<tr>
<td>(\text{MnMg}_5\text{O}_6)</td>
<td>5b</td>
<td>Sextet</td>
<td>0.000</td>
<td>1.015</td>
<td>4.95</td>
</tr>
<tr>
<td>(\text{MnMg}_6\text{O}_7)</td>
<td>5c</td>
<td>Sextet</td>
<td>0.569</td>
<td>0.321</td>
<td>4.74</td>
</tr>
<tr>
<td>(\text{MnMg}_7\text{O}_8)</td>
<td>5d</td>
<td>Sextet</td>
<td>0.645</td>
<td>0.762</td>
<td>5.00</td>
</tr>
<tr>
<td>(\text{MnMg}_8\text{O}_9)</td>
<td>5e</td>
<td>Sextet</td>
<td>0.690</td>
<td>0.980</td>
<td>4.99</td>
</tr>
<tr>
<td>(\text{MnMg}<em>9\text{O}</em>{10})</td>
<td>6</td>
<td>Sextet</td>
<td>0.692</td>
<td>0.990</td>
<td>4.99</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{10}\text{O}</em>{11})</td>
<td>7a</td>
<td>Sextet</td>
<td>0.000</td>
<td>1.499</td>
<td>4.99</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{11}\text{O}</em>{12})</td>
<td>7b</td>
<td>Sextet</td>
<td>0.000</td>
<td>1.083</td>
<td>5.00</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{12}\text{O}</em>{13})</td>
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<td>Sextet</td>
<td>0.161</td>
<td>0.942</td>
<td>4.95</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{13}\text{O}</em>{14})</td>
<td>7d</td>
<td>Sextet</td>
<td>0.091</td>
<td>0.444</td>
<td>5.00</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{14}\text{O}</em>{15})</td>
<td>8a</td>
<td>Sextet</td>
<td>0.000</td>
<td>1.377</td>
<td>4.99</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{15}\text{O}</em>{16})</td>
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<td>Sextet</td>
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<td>1.603</td>
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<tr>
<td>(\text{MnMg}<em>{16}\text{O}</em>{17})</td>
<td>9a</td>
<td>Sextet</td>
<td>1.527</td>
<td>0.917</td>
<td>1.09</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{17}\text{O}</em>{18})</td>
<td>9b</td>
<td>Sextet</td>
<td>0.118</td>
<td>1.420</td>
<td>5.00</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{18}\text{O}</em>{19})</td>
<td>10a</td>
<td>Sextet</td>
<td>1.645</td>
<td>0.721</td>
<td>1.13</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{19}\text{O}</em>{20})</td>
<td>10b</td>
<td>Sextet</td>
<td>0.064</td>
<td>1.273</td>
<td>4.98</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{20}\text{O}</em>{21})</td>
<td>10c</td>
<td>Sextet</td>
<td>0.000</td>
<td>1.401</td>
<td>4.99</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{21}\text{O}</em>{22})</td>
<td>10d</td>
<td>Sextet</td>
<td>0.237</td>
<td>1.205</td>
<td>4.98</td>
</tr>
<tr>
<td>(\text{MnMg}<em>{22}\text{O}</em>{23})</td>
<td>10e</td>
<td>Sextet</td>
<td>0.000</td>
<td>1.499</td>
<td>4.99</td>
</tr>
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six-number ring with the magnetic moment of 4.99 $\mu_B$. Compared with $(\text{MgO})_6$ ($D_{3d}$), it displays a lower symmetry $C_s$. The lowest-energy structure of MnMg$_6$O$_7$ cluster is 7a, and its magnetic moment is 5.00 $\mu_B$. Another isomer 7c with $\Delta E=0.091$ eV comes next in energy. The remaining isomer (7b) obtained in the structural optimization of MnMg$_6$O$_7$ with $\Delta E=0.161$ eV is less stable than the isomer (7a). For MnMg$_7$O$_8$, it is in a sextet state with high energy gap of 1.377 eV and large magnetic moment of 4.99 $\mu_B$. MnMg$_8$O$_9$ cluster prefers 9a with $C_s$ symmetry corresponding to $\mu=5.00$ $\mu_B$ as ground state. It is obtained by replacing one Mg atom of the outer-layer hexagon of $(\text{MgO})_9$ cluster with an Mn atom. The other isomer (9b) with $C_{2v}$ symmetry is found using one Mn atom substituting for one Mg atom of the inner-layer hexagon of $(\text{MgO})_9$ cluster, and 1.527 eV above the lowest-energy structure. For the case of $n=10$, 10d, the total magnetic moment of 4.99 $\mu_B$ is the most stable doping structure. The 10a, 10b, 10c, and 10e isomers with $\Delta E$ changing from 0.064 eV to 1.645 eV have lower stability. It can be seen from the structures in Fig.1 that one Mn impurity atom does not change the basic geometric configurations of magnesia clusters except for some local structural distortions. Moreover, we find that the Mn atom prefers to replace the Mg atom which has low coordination number (two coordination number for $n=2$, 3, and 5, three coordination number for $n=4$, 6, 8, 9, and 10) in all

FIG. 1 The isomers of MnMg$_{n-1}$O$_n$ ($n=2\text{--}10$) clusters, and the ground-state structures of pure $(\text{MgO})_n$ ($n=2\text{--}10$) clusters have been listed. The green, red and purple balls represent Mg, O and Mn atoms, respectively. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.
the lowest-energy MnMg$_{n-1}$O$_n$ ($n=2$–$10$) structures. Compared with pure (MgO)$_n$ clusters, the symmetry of Mn-doped magnesia clusters clearly decreases except for MnMg$_4$O$_5$ (5a).

**B. Bond lengths and Mayer bond orders**

Although a number of isomers are identified for some cluster sizes, we only give a detailed discussion of the lowest-energy structures of MnMg$_{n-1}$O$_n$. The bond lengths and Mayer bond orders of the lowest-energy structures of (MgO)$_n$ and MnMg$_{n-1}$O$_n$, can be found in Table II. The average Mg–O bond lengths in pure (MgO)$_n$ clusters are in the range of 1.847 Å to 1.980 Å, while the corresponding average Mg–O bond lengths are optimized at 1.852–2.023 Å in the MnMg$_{n-1}$O$_n$ clusters. These results clearly indicate that the doping of Mn atom has increased the average Mg–O bond lengths compared with that of pure (MgO)$_n$ clusters. In addition, the average Mn–O bond lengths in MnMg$_{n-1}$O$_n$ clusters fall in the range of 1.712 Å to 2.012 Å. This result is in accordance with the earlier DFT calculation results from Nayak et al., who found that the calculated Mn–O bond lengths are 1.650–2.070 Å in MnO$_n$ clusters [40]. From Table II, we also see that the average Mayer bond orders between the Mg atom and O atom are in the range of 0.404–0.843 for pure (MgO)$_n$ clusters. For MnMg$_{n-1}$O$_n$, the average Mayer bond orders between the Mg atom and O atom vary from 0.414 to 0.796, whereas the average Mayer bond orders between the Mn atom and O atom are 0.713–1.570. It is obvious that the average Mayer bond orders between the Mg atom and O atom present a decreasing trend in each cluster size for MnMg$_{n-1}$O$_n$, compared with that for the corresponding pure (MgO)$_n$. Especially, it is worth pointing out that the average Mg–O bond lengths and the average Mayer bond orders between the Mg atom and O atom exhibit a reverse change trend either for pure (MgO)$_n$ clusters or MnMg$_{n-1}$O$_n$ cluster. Similarly, this characteristic can be observed between the average Mn–O bond lengths and the average Mayer bond orders between the Mn atom and O atom in each size MnMg$_{n-1}$O$_n$ clusters. In general, a short bond length signifies strong bonding ability for the same bond kind. Thus, from the above analysis, we can come to the conclusion that the larger the Mayer bond order, the stronger the bond between the atoms in clusters is.

**C. Stabilities of the lowest-energy MnMg$_{n-1}$O$_n$ clusters**

For the purpose of analyzing the stabilities of the lowest-energy Mn-doped configurations, the average binding energies have been computed. We define the average binding energy (BE) of (MgO)$_n$ and MnMg$_{n-1}$O$_n$ clusters as:

\[
\text{BE}_1 = \frac{1}{2n} (nE_{\text{Mg}} + nE_{\text{O}} - E_{\text{total}}) \tag{1}
\]

\[
\text{BE}_2 = \frac{1}{2n} [(n-1)E_{\text{Mg}} + nE_{\text{O}} + E_{\text{Mn}} - E_{\text{total}}] \tag{2}
\]

where $E_{\text{Mg}}$, $E_{\text{O}}$, and $E_{\text{Mn}}$ represent the energies of isolated Mg, O, and Mn atoms, respectively; $E_{\text{total}}$ represents the total energies of the system, and $n$ represents the size of clusters. The second order difference of cluster energies ($\Delta^2E$) is often used to measure the relative stability of clusters. Therefore, we also calculate the $\Delta^2E$ of (MgO)$_n$ and MnMg$_{n-1}$O$_n$ clusters by the following equations:

\[
\Delta^2E_1 = E_{(\text{MgO})_{n+1}} + E_{(\text{MgO})_{n-1}} - 2E_{(\text{MgO})_n} \tag{3}
\]

\[
\Delta^2E_2 = E_{\text{MnMg}_n\text{O}_{n+1}} + E_{\text{MnMg}_{n-2}\text{O}_{n-1}} - 2E_{(\text{MnMg}_{n-1}\text{O}_n)} \tag{4}
\]

where $E_i$ stands for the total energy of corresponding $i$ system. The calculation results of average binding energies are plotted in Fig.2(a) as a function of cluster size. Clearly, both the average binding energies of (MgO)$_n$ and MnMg$_{n-1}$O$_n$ clusters monotonically increase with the growth of cluster size except for

<table>
<thead>
<tr>
<th>$n$</th>
<th>$R_{\text{MgO}}$/Å</th>
<th>$R_{\text{MnO}}$/Å</th>
<th>$\text{MBO}_1$</th>
<th>$\text{MBO}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.888</td>
<td>2.023</td>
<td>1.712</td>
<td>0.843</td>
</tr>
<tr>
<td>3</td>
<td>1.847</td>
<td>1.852</td>
<td>1.845</td>
<td>0.841</td>
</tr>
<tr>
<td>4</td>
<td>1.972</td>
<td>1.973</td>
<td>2.012</td>
<td>0.546</td>
</tr>
<tr>
<td>5</td>
<td>1.949</td>
<td>1.968</td>
<td>1.838</td>
<td>0.587</td>
</tr>
<tr>
<td>6</td>
<td>1.921</td>
<td>1.953</td>
<td>2.004</td>
<td>0.546</td>
</tr>
<tr>
<td>7</td>
<td>1.955</td>
<td>1.956</td>
<td>2.002</td>
<td>0.544</td>
</tr>
<tr>
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<td>1.946</td>
<td>1.998</td>
<td>0.404</td>
</tr>
<tr>
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<td>1.980</td>
<td>1.984</td>
<td>1.983</td>
<td>0.488</td>
</tr>
<tr>
<td>10</td>
<td>1.943</td>
<td>1.944</td>
<td>1.980</td>
<td>0.545</td>
</tr>
</tbody>
</table>

**TABLE II** The average Mg–O and Mn–O bond lengths, the Mayer bond orders between Mg and O atoms (MBO 1) and between Mn and O atoms (MBO 2) in the lowest-energy structures of (MgO)$_n$ clusters and MnMg$_{n-1}$O$_n$ clusters ($n=2$–$10$).
related to the stability of pure (MgO)\(_n\) at energy in Fig. 2(a). Furthermore, the \(\Delta E\) findings are well confirmed by the average binding the highest stability in the Mn-doped clusters. These clusters, indicating that the MnMg\(_{8n}\) consistent with the mass spectra [11] of MgO clusters. We can see that the positive \(\Delta E\) and Mn-doped clusters as a function of cluster size. An important observation is that the average binding to the pure (MgO)\(_n\) energies of the doped clusters increase as compared to MnMg\(_{8n}\)\(_O\) clusters, the local peaks of \(\Delta E\) are found at cluster size of \(n=4, 6,\) and 9 for pure (MgO)\(_n\), while the negative \(\Delta E\) occur at \(n=3, 5, 7,\) and 8, which is well consistent with the mass spectra [11] of MgO clusters. For MnMg\(_{8n-1}\)O\(_n\) clusters, the local peaks of \(\Delta E\) are found at \(n=6\) and 9, while the local minima occur at \(n=5\) and 7. These findings indicate that MnMg\(_{6}\)O\(_6\) and MnMg\(_{8}\)O\(_6\) exhibit higher stability than their neighboring clusters. In particular, the conspicuous maximum of \(\Delta E\) localizes at \(n=9\) for MnMg\(_{8n-1}\)O\(_n\) clusters, indicating that the MnMg\(_{8}\)O\(_6\) cluster keeps the highest stability in the Mn-doped clusters. These findings are well confirmed by the average binding energy in Fig.2(a). Furthermore, the \(\Delta E\) of pure and doped clusters in Fig.2(b) reveal the same high stability at \(n=6\) and 9, implying the stability of MnMg\(_{8n-1}\)O\(_n\) is related to the stability of pure (MgO)\(_n\) clusters.

\[BE = \text{Average binding energy} \]  
\[\Delta E = \text{Second order difference of cluster energy} \]

\(n=2\) to \(n=10\). This result reflects the fact that with increasing the cluster size, the stability of the cluster increases in the cluster sizes of \(n=2\) to 9. An important observation is that the average binding energies of the doped clusters increase as compared to the pure (MgO)\(_n\) clusters. Figure 2(b) shows the second order difference of cluster energies for (MgO)\(_n\) and Mn-doped clusters as a function of cluster size. We can see that the positive \(\Delta E\) are found at cluster size of \(n=4, 6,\) and 9 for pure (MgO)\(_n\), while the negative \(\Delta E\) occur at \(n=3, 5, 7,\) and 8, which is well consistent with the mass spectra [11] of MgO clusters. For MnMg\(_{8n-1}\)O\(_n\) clusters, the local peaks of \(\Delta E\) are found at \(n=6\) and 9, while the local minima occur at \(n=5\) and 7. These findings indicate that MnMg\(_{6}\)O\(_6\) and MnMg\(_{8}\)O\(_6\) exhibit higher stability than their neighboring clusters. In particular, the conspicuous maximum of \(\Delta E\) localizes at \(n=9\) for MnMg\(_{8n-1}\)O\(_n\) clusters, indicating that the MnMg\(_{8}\)O\(_6\) cluster keeps the highest stability in the Mn-doped clusters. These findings are well confirmed by the average binding energy in Fig.2(a). Furthermore, the \(\Delta E\) of pure and doped clusters in Fig.2(b) reveal the same high stability at \(n=6\) and 9, implying the stability of MnMg\(_{8n-1}\)O\(_n\) is related to the stability of pure (MgO)\(_n\) clusters.

\[BE = \text{Average binding energy} \]  
\[\Delta E = \text{Second order difference of cluster energy} \]

\(n=2\) to \(n=10\). This result reflects the fact that with increasing the cluster size, the stability of the cluster increases in the cluster sizes of \(n=2\) to 9. An important observation is that the average binding energies of the doped clusters increase as compared to the pure (MgO)\(_n\) clusters. Figure 2(b) shows the second order difference of cluster energies for (MgO)\(_n\) and Mn-doped clusters as a function of cluster size. We can see that the positive \(\Delta E\) are found at cluster size of \(n=4, 6,\) and 9 for pure (MgO)\(_n\), while the negative \(\Delta E\) occur at \(n=3, 5, 7,\) and 8, which is well consistent with the mass spectra [11] of MgO clusters. For MnMg\(_{8n-1}\)O\(_n\) clusters, the local peaks of \(\Delta E\) are found at \(n=6\) and 9, while the local minima occur at \(n=5\) and 7. These findings indicate that MnMg\(_{6}\)O\(_6\) and MnMg\(_{8}\)O\(_6\) exhibit higher stability than their neighboring clusters. In particular, the conspicuous maximum of \(\Delta E\) localizes at \(n=9\) for MnMg\(_{8n-1}\)O\(_n\) clusters, indicating that the MnMg\(_{8}\)O\(_6\) cluster keeps the highest stability in the Mn-doped clusters. These findings are well confirmed by the average binding energy in Fig.2(a). Furthermore, the \(\Delta E\) of pure and doped clusters in Fig.2(b) reveal the same high stability at \(n=6\) and 9, implying the stability of MnMg\(_{8n-1}\)O\(_n\) is related to the stability of pure (MgO)\(_n\) clusters.

\[BE = \text{Average binding energy} \]  
\[\Delta E = \text{Second order difference of cluster energy} \]

\(n=2\) to \(n=10\). This result reflects the fact that with increasing the cluster size, the stability of the cluster increases in the cluster sizes of \(n=2\) to 9. An important observation is that the average binding energies of the doped clusters increase as compared to the pure (MgO)\(_n\) clusters. Figure 2(b) shows the second order difference of cluster energies for (MgO)\(_n\) and Mn-doped clusters as a function of cluster size. We can see that the positive \(\Delta E\) are found at cluster size of \(n=4, 6,\) and 9 for pure (MgO)\(_n\), while the negative \(\Delta E\) occur at \(n=3, 5, 7,\) and 8, which is well consistent with the mass spectra [11] of MgO clusters. For MnMg\(_{8n-1}\)O\(_n\) clusters, the local peaks of \(\Delta E\) are found at \(n=6\) and 9, while the local minima occur at \(n=5\) and 7. These findings indicate that MnMg\(_{6}\)O\(_6\) and MnMg\(_{8}\)O\(_6\) exhibit higher stability than their neighboring clusters. In particular, the conspicuous maximum of \(\Delta E\) localizes at \(n=9\) for MnMg\(_{8n-1}\)O\(_n\) clusters, indicating that the MnMg\(_{8}\)O\(_6\) cluster keeps the highest stability in the Mn-doped clusters. These findings are well confirmed by the average binding energy in Fig.2(a). Furthermore, the \(\Delta E\) of pure and doped clusters in Fig.2(b) reveal the same high stability at \(n=6\) and 9, implying the stability of MnMg\(_{8n-1}\)O\(_n\) is related to the stability of pure (MgO)\(_n\) clusters.

D. Electronic structures and chemical bonds

The Mulliken charge distributions for both the lowest-energy (MgO)\(_n\) and Mn-doped (MgO)\(_n\) clusters are given in Supplementary material (shown in Fig.S1). Especially, the Mulliken atomic charges of MnMg\(_{8n-1}\)O\(_n\) clusters are shown in Fig.3. It is clearly observed from Fig.S1 that the charges are all redistributed when a single Mn atom is doped into the (MgO)\(_n\) clusters. The charges on all the Mn atoms are positive. A pronounced difference is observed for atomic charges between (MgO)\(_2\) and MnMg\(_2\O\(_2\). The dopant Mn atom in (MgO)\(_2\) leads to the Mulliken charge of Mg atom change from 0.927 \(e\) to 0.669 \(e\) and the charge of O atoms to change from \(0.927\) \(e\) to \(0.651\) \(e\). In all the doped clusters the charges of Mn atoms change within the range of 0.564 \(e\) to 0.664 \(e\), which are smaller than 0.690–0.840 \(e\) in (MnO)\(_n\) clusters presented by Nayak et al. [40].

In order to investigate the nature of the bond in the lowest-energy MnMg\(_{8n-1}\)O\(_n\) clusters, the deformation electronic density is performed, which is denoted as the difference between the total electron density of the system and the electron density of the isolated...
TABLE III Charge transferred from the Mg atoms to the O atoms and from Mn atom to the O atoms, local magnetic moment, and charge transferred from one orbital to another orbital in the MnMg$_2$O$_3$ cluster (the direction of electron spin is represented by the arrow in parentheses).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge/</th>
<th>e</th>
<th></th>
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<td></td>
</tr>
<tr>
<td>Mg1</td>
<td>1.002</td>
<td>−0.006</td>
<td>0.176(↑)</td>
<td>0.184(↑)</td>
<td>0.213(↑)</td>
<td>0.212(↑)</td>
<td>0.109(↑)</td>
<td>0.107(↑)</td>
</tr>
<tr>
<td>O2</td>
<td>−0.950</td>
<td>0.014</td>
<td>0.939(↑)</td>
<td>0.938(↑)</td>
<td>2.538(↑)</td>
<td>2.525(↑)</td>
<td>0.004(↑)</td>
<td>0.004(↑)</td>
</tr>
<tr>
<td>Mg3</td>
<td>1.002</td>
<td>−0.005</td>
<td>0.176(↑)</td>
<td>0.185(↑)</td>
<td>0.213(↑)</td>
<td>0.212(↑)</td>
<td>0.109(↑)</td>
<td>0.107(↑)</td>
</tr>
<tr>
<td>O4</td>
<td>−0.819</td>
<td>0.152</td>
<td>0.937(↑)</td>
<td>0.941(↑)</td>
<td>2.540(↑)</td>
<td>2.386(↑)</td>
<td>0.007(↑)</td>
<td>0.005(↑)</td>
</tr>
<tr>
<td>O5</td>
<td>−0.819</td>
<td>0.152</td>
<td>0.937(↑)</td>
<td>0.941(↑)</td>
<td>2.541(↑)</td>
<td>2.387(↑)</td>
<td>0.007(↑)</td>
<td>0.005(↑)</td>
</tr>
<tr>
<td>Mn6</td>
<td>0.584</td>
<td>4.677</td>
<td>0.491(↑)</td>
<td>0.116(↑)</td>
<td>0.247(↑)</td>
<td>0.138(↑)</td>
<td>4.805(↑)</td>
<td>0.614(↑)</td>
</tr>
</tbody>
</table>

Fig. 4 HOMO-LUMO energy gaps ($E_g$) for the lowest-energy MnMg$_{n-1}$O$_n$ ($n=2-10$) clusters as a function of cluster size.

atom. The detailed results for MnMg$_{n-1}$O$_n$ clusters with $n=2$, 3, 4, and 5 are plotted in Fig.3, and the results of other MnMg$_{n-1}$O$_n$ clusters ($n=6$, 7, 8, 9, and 10) are presented in Fig.S2 in Supplementary material. The deformation density marked by blue demonstrates a charge transfer from the region (Mn/Mg sites), while that marked by red demonstrates a high charge accumulation in the region (O sites). We can see that both the blue and red exist around the Mn atoms. Thus, the covalent bonding character is exhibited between Mn and O atoms, which is in accordance with the large average Mayer bond orders (0.713−0.796) in Table II. The nature of bonding between Mg and O atom is found partly ionic (seen in Fig.3 and Figure S2) as confirmed by the small Mayer bond orders (0.414−0.796) in Table II.

The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is a useful quantity for examining the electronic properties of clusters. In this work, the HOMO-LUMO energy gaps ($E_g$) of the lowest-energy MnMg$_{n-1}$O$_n$ ($n=2-10$) have been calculated. The computed results are shown in Fig.4 as a function of cluster size. Interestingly, three conspicuous maxima are found at $n=3$, 6, 9. As illustrated in Fig.4, for cluster size in the range of $n=2-5$, MnMg$_2$O$_3$ cluster has the largest energy gap (1.271 eV), while MnMgO$_2$ cluster has the smallest energy gap (0.707 eV). In contrast, for cluster sizes ranging from $n=6$ to $n=10$, MnMg$_3$O$_9$ cluster has the largest energy gap (1.603 eV), while MnMg$_6$O$_7$ cluster has the smallest energy gap (1.083 eV).

### E. Magnetic properties

The total magnetic moments of the lowest-energy structures of MnMg$_{n-1}$O$_n$ clusters are shown in Table I. Figure 5 shows the local magnetic moments on the typical MnMg$_{n-1}$O$_n$ ($n=3$, 6, and 9) clusters. From Table I one can see that MnMg$_{n-1}$O$_n$ clusters are all magnetic. High magnetic moments of $\sim 5 \mu_B$ are found at all the lowest energy structures with the exception of $n=2$ which has 3.00 $\mu_B$. It can be noted from Fig.5 that the magnetism of these clusters is mainly from the contribution of the dopant Mn atoms, and a small amount of moments are found on Mg and O atoms. Other clusters have high magnetic moments of $\sim 5 \mu_B$ which are mainly from the contribution of the O and the dopant Mn atoms. Thus, it can explain the origin of this large value of 3 $\mu_B$ found for MnMgO$_2$. To gain more insight into the magnetic nature of these three clusters, the local magnetic moment and charge transfer in the MnMg$_2$O$_3$ cluster are listed in Table III. The total magnetic moment of MnMg$_2$O$_3$ is 4.98 $\mu_B$, in which 4.68 $\mu_B$ is from Mn atom, while $-0.01 \mu_B$ is from two Mg atoms and 0.32 $\mu_B$ is from three O atoms. This confirms that the magnetism of this cluster mostly stems from the doping of Mn atom. In addition, it is found that the local magnetic moments on each atom are not integer because of the covalent bonding in MnMg$_2$O$_3$ cluster. The same phenomenon is presented in transition metal doped (ZnO)$_{12}$ clusters [41]. According to Table III there is a charge transfer of 2.588 $|e|$ from Mg and Mn atoms to three O atoms. It is worth noting that the O atoms labeled with Arabic numeral 4 and 5 (signed in Fig.5) are in the vicinity of the Mn atom. They gain less charge (0.819 $|e|$ each) than the O atom labeled with 2 (0.950 $|e|$). Their contribution to magnetic moment is 0.30 $\mu_B$, which is larger than the contribution of the O atom labeled with Arabic numeral 2 (0.01 $\mu_B$). We can
deduce that the position of the atoms in the structure
has great effect on the charge transfer and magnetism
for the atoms in MnMgO3 cluster. Furthermore, the
electronic configuration of Mn atom is 3d^44s^2. Com-
bined with Table III, it can be found that the 3d and
4p orbitals of the Mn atom get additional charge (about
0.420 and 0.390 e, respectively), whereas its 4s orbital
lose about 1.600 e. This fact indicates that Mn4s elec-
trons partially transfer to Mn 4p and 3d orbitals and
also to their neighboring O atoms. Meanwhile, about
two Mn3d electrons spin up which results in the high lo-
cal magnetism at the Mn atom. At the same time, there
are some charge transfers from Mg3s orbitals to Mg3p
orbitals and their neighboring O atoms. Because of the
charge transfer between these atoms, the corresponding
interaction occurs accompanying the formation of local
magnetism.

In order to further understand the magnetic nature
of the considered clusters, we investigate the s-, p-, and
d-projected density of states (PDOS) of majority-spin
and minority-spin for MnMgO3 cluster. The result is
shown in Fig.6. It is clearly seen from Fig.6 that the
total DOS at the Fermi level consist mainly of Mn3d
and O2p states. Clearly, the up states near the Fermi
level are missing for the down component, resulting in a
large total magnetic moment (5.00 µB) for MnMgO3.
In other words, the splitting between the alpha and
beta states near fermi level in the Mn projected DOS
plot reveals magnetism in MnMgO3 cluster. For O
atoms, the main contribution to the magnetism comes
from the p-projected DOS near the Fermi level. For Mg
atoms, the contributions of moments are primarily from
s-projected DOS in the energy region of 1.0−7.0 eV
with a small amount of p-projected DOS. It is obvi-
ously shown that the d-projected DOS plays dominant
roles in the energy region of −5.0 eV to 7.0 eV for Mn
atom, whereas the s- and p-projected DOS have smaller
contributions.

IV. CONCLUSION

We optimize the geometric structures of pure and
Mn-doped magnesia clusters by DFT calculations. It
is found that the Mn atom prefers to replace the Mg
atom which has low coordination number (two coordi-
nation number for n=2, 3, and 5, three coordination
number for n=4, 6, 8, 9, and 10) in all the lowest-
ergy MnMg_{n-1}O_n (n=2−10) structures. The stability
analysis clearly shows that both the average bind-
ing energies of (MgO)_n and MnMg_{n-1}O_n monotonically
increase with the growth of cluster size except for (MgO)_10. The second order energy differences of
MnMg_{n-1}O_n indicate that MnMgO_6, and MnMgO_9
clusters have a higher relative stability than the neigh-
boring ones. All the Mn-doped magnesia clusters ex-
hibit a high total magnetic moments with the exception
of n=2 which has 3.00 µB. High magnetic moments of
~5 µB are found for MnMg_{n-1}O_n clusters with the ex-
ception of n=2 which has 3.00 µB. The magnetism of

FIG. 5 The local magnetic moment on each atom of the relative stably MnMg_{n-1}O_n (n=3, 6, and 9) structures. The
number label for MnMgO_3 is also shown in the figure.

FIG. 6 The s-, p-, and d-projected density of states (PDOS) of majority-spin and minority-spin of the most stable
MnMgO_3 cluster. All the Fermi energies are set at zero.
these clusters is mainly from the contribution of the dopant Mn atoms. Furthermore, the charge transfer analysis confirms that the magnetism of these clusters mostly stems from the dopant Mn atoms.

V. ACKNOWLEDGEMENTS

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Supplementary material: Figures of Mulliken atomic charges and deformation electronic density are given. The lattice constants of MnMg$_{60-\Omega_n}$ clusters when we calculated the electronic density of states are presented.