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Engineering the magnetic properties of the Mn_{13} cluster by doping

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With a goal to produce a giant magnetic moment in a Mn_{13} cluster that will be useful for practical applications, we have considered the structure and magnetic properties of a pure Mn_{13} cluster and substitutionally doped it with X = Ti, V, Cr, Fe, Co, Ni atom respectively to produce Mn_{12}X clusters. We find that Ti and V substitutions in a Mn_{13} cluster are the most promising in terms of gaining substantial binding energy as well as achieving a higher magnetic moment through ferromagnetic alignment of the atom-centered magnetic moments. This has been demonstrated in terms of energetics and electronic properties of the clusters. For comparison, we have also studied the effect of N capping of Mn_{13} cluster, predicted in an earlier work [Phys. Rev. Lett. 89, 185504 (2002)], as a means of producing stable giant magnetic moments in Mn clusters up to cluster sizes of five Mn atoms.

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I. INTRODUCTION

The behavior of manganese is very special both in bulk and cluster forms. The electronic configuration of the atom has a half-filled 3d shell and a filled 4s shell. Structural and magnetic properties of manganese clusters have been studied in the past. 1−7 It has been shown 1−5 that small Mn clusters containing up to four to five atoms exhibit ferromagnetic coupling of individual atomic magnetic moments, with a magnetic moment per atom comparable with the magnetic moment of Mn at the atomic limit, which is 5μ_B. Interestingly, the coupling becomes ferrimagnetic as the cluster size increases and the net magnetic moment falls abruptly, as shown in experimental works 8,9 and also supported by the first-principles studies. 10 The atom-centered individual magnetic moment, though, remains of the order of atomic moment. Therefore, it will be of great technological interest if the ferrimagnetic coupling can be transformed into a ferromagnetic coupling, thereby resulting in a giant magnetic moment. One way to accomplish this is by doping. 11 Furthermore, if the doping also increases the stability of the cluster compared to the pure Mn cluster of the same size, then it will be an additional achievement on top of spin engineering. Such clusters will be promising building blocks for making new cluster-assembled materials. Along the same line of thought, Rao and Jena 12 previously studied the structure and magnetism of N-capped Mn clusters. Based on their study carried out on Mn clusters of sizes up to five Mn atoms, they proposed that N capping can be used as a viable means to enhance both the stability and the ferromagnetic coupling among Mn atoms in a Mn cluster. In the present work, we have proposed an alternative route and studied systematically the effect of substitutional doping of a Mn_{13} cluster to produce Mn_{12}X clusters with X = Ti, V, Cr, Fe, Co, Ni atoms. We find that Ti and V substitutions are the most effective as both the magnetic moment and stability increase significantly for the Mn_{12}Ti and Mn_{12}V clusters as compared to the pure Mn_{13} cluster. To compare our finding with the proposal of Rao and Jena 12 through N capping, we have also studied the structure and electronic properties of the Mn_{13}N cluster. Although, the N capping enhances the stability and magnetic moment as compared to a pure Mn_{13} cluster, the gain in total magnetic moment is found to be smaller as compared to that of Mn_{12}Ti and Mn_{12}V clusters. Also the substitutional Ti doping and V doping are more interesting because they keep the volume of the cluster intact, as opposed to N capping, which increases the volume of the original clusters. The rest of the paper is organized in the following manner. Section II describes the computational details. Section III summarizes the results obtained in our study. Section III A is devoted to the results describing a pure Mn_{13} cluster. Sections III B and III C are devoted to results on Mn_{12}X clusters. In Sec. III D, we analyze the origin of enhanced stability and magnetic moments in Mn_{12}X clusters. Section III E describes our comparative study on a N-capped Mn_{13} cluster. We end the paper with a conclusion in Sec. IV.

II. COMPUTATIONAL DETAILS

Our calculations have been performed using density-functional theory, within the pseudopotential plane-wave method as implemented in the Vienna ab initio simulation package. 13 We have used the projector augmented-wave pseudopotentials 14,15 and the Perdew-Bruke-Emzerhof exchange-correlation functional 16 for spin-polarized generalized gradient approximations. The wave functions were expanded in the plane-wave basis set with a kinetic energy cutoff of 270 eV, and reciprocal space integrations were carried out at the Γ point. Symmetry-unrestricted geometry optimization has been performed using the conjugate gradient and the quasi-Newtonian methods until all the force components became less than a threshold value of 0.005 eV/Å. Although the noncollinear effect of atomic spins is significant for Mn clusters, it has been shown in the earlier work 17 that for a Mn_{13} cluster, the degree of noncollinearity is very small. Therefore, we have optimized the structures for all the spin multiplicities M = 2S + 1 under the approximation of a collinear atomic spin arrangement to determine the magnetic moment of the minimum energy structure. Simple cubic supercells were used with the periodic boundary conditions, where two neighboring clusters were kept separated by at least 12 Å vacuum space to make the interaction between the cluster images negligible.
The binding energy ($E_B$) of each Mn$_{12}$X cluster has been calculated with respect to the free atoms as

$$E_B(\text{Mn}_{12}X) = 12E(\text{Mn}) + E(X) - E(\text{Mn}_{12}X),$$

(1)

where $E(\text{Mn}_{12}X)$, $E(\text{Mn})$, and $E(X)$ are the total energies of the Mn$_{12}$X cluster, an isolated Mn atom, and an isolated X atom, respectively. We also have analyzed the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the magnetic clusters by defining the spin gap as follows:

$$\delta_1 = -[\epsilon_{\text{majority}}^\text{HOMO} - \epsilon_{\text{minority}}^\text{LUMO}],$$

$$\delta_2 = -[\epsilon_{\text{minority}}^\text{HOMO} - \epsilon_{\text{majority}}^\text{LUMO}].$$

(2)

The system is considered to be stable if both $\delta_1$ and $\delta_2$ are positive. A detailed discussion about $\delta_1$ and $\delta_2$ can be found elsewhere [18–21].

III. RESULTS AND DISCUSSIONS

A. Pure Mn$_{13}$ cluster

Because the transition-metal clusters generally prefer compact geometry to maximize the interaction between the rather localized d-d orbitals, we have considered icosahedral, cube-octahedral, and hexagonal-close-packed (hcp) structures as the most probable starting geometries to determine the minimum energy structure (MES) for Mn$_{13}$ clusters. These three are the most compact and highly coordinated structures for the 13-atom cluster. Each structure was allowed to relax for all possible collinear spin configurations of the atoms. Figure 1 shows the variation of total binding energy as a function of total magnetic moments for these three structures of a Mn$_{13}$ cluster.

We found that an icosahedral structure with a total magnetic moment of $3\mu_B$ and a total binding energy of 28.023 eV is the MES for the Mn$_{13}$ cluster, as predicted earlier. An icosahedron of 13 atoms can be viewed as consisting of two pentagonal rings connected with each other through the central atom and capped with two apex atoms at its ends, as shown in Fig. 2. We also observed a spin-segregated state of atomic moments in the MES of a Mn$_{13}$ cluster in the sense that the atoms within each of the two pentagonal rings of an icosahedral Mn$_{13}$ cluster are ferromagnetically aligned, while the two pentagonal rings are antiferromagnetically coupled with each other (cf. Fig. 2). This is in agreement with the previous report by another group.

B. Energetics of Mn$_{12}$X clusters

For the calculations reported in the following, we have considered doped Mn$_{12}$X clusters of icosahedral symmetry with the impurity X atom sitting at the center of the icosahedron and optimized it for all possible collinear spin configurations of atoms. We have considered six different substitutions at the central Mn site of Mn$_{13}$ cluster: considering the substituting X atom as one of the three elements to the left of Mn in the Periodic Table (Ti, V, Cr) and one of the three elements to the right of Mn in the Periodic Table (Fe, Co, Ni). This assumed geometry of icosahedral symmetry with the impurity X atom sitting at the center of the icosahedron needs some discussion. In our earlier work on V-doped Co clusters, we have also shown by an ab initio molecular dynamics study that the ground-state structure of Co$_{12}$V cluster adopts an icosahedral pattern, with the substituting V atom always preferring to sit at the central site of the icosahedral Co$_{12}$V cluster. Theoretical works on clusters of icosahedral symmetry with substitution at the central site have been reported for MC$_{12}$ ($M = T i, V, C r, M n, F e, C o, N i$) clusters, Fe$_{12}$M ($M = B e, O, M g, A l, S i, S, T i, M n, F e, N i, Z n, S e, P d$) clusters, and Al$_{12}$M ($M = B, A l, G a, C, S i, G e, T i, A s$) clusters. Therefore, there exist enough reports in the literature considering the substitution at the central site by atoms of similar or larger sizes, justifying our choice of the impurity X atom doped at the central site of an icosahedral Mn$_{13}$ cluster. Furthermore, as discussed later in Sec. III D, Mn-X dimers were found to have higher binding energies as compared to a Mn$_2$ dimer. This in turn would indicate that single-atom substitution of Mn by an X atom will prefer a configuration where the number of Mn-X bonds are maximized, which is possible for substitution at the central position. Our total energy calculations by putting the
substituting atoms at different sites of the icosahedral Mn13 cluster support this idea.

Figure 3 shows the plot of binding energies as a function of total magnetic moments (N ↑−N ↓) of all the Mn12X clusters. In order to see the effect of substitutional doping distinctly, we have plotted the binding energy for each spin multiplet of Mn12X clusters with respect to that of the MES for a pure Mn13 cluster, i.e., \( E_B(Mn12X) - E_B(Mn13)_{MES} \). The positive value of this quantity means a gain in binding energy upon substitutional doping. It is seen from Fig. 3(a) that gains in binding energies are achieved in the case of Ti and V substitutions for a range of values of total magnetic moments, from \( \sim 2 \mu_B \) to \( \sim 50 \mu_B \). However, for Cr substitution there is no gain in binding energy except for a small gain for the magnetic moments of \( 22 \mu_B \) and \( 10 \mu_B \). On the other hand, for Fe, Co, and Ni substitutions, there is again gain in binding energy for each of them up to a total magnetic moment of \( \sim 30 \mu_B \), as seen from Fig. 3(b). Notice that these gains are not as high as we observed in the case of Ti and V substitutions. However, they are better than the Cr substitution.

### C. Energetics and magnetic moments of MESs of Mn12X clusters

Table I shows the total binding energies and total magnetic moments of the MESs of Mn12X clusters. It is seen that the MESs of all the doped clusters have higher binding energies and magnetic moments as compared to those of the MES for a Mn13 cluster. We note again that the MESs of the Mn12Ti and Mn12V clusters have significantly higher binding energies than Mn13. Similarly, the total magnetic moments are found to be significantly large for the MESs of clusters doped with elements to the left of Mn in the Periodic Table. Moreover, there are several isomers [as seen from Fig. 3(a)] of Mn12Ti and Mn12V clusters with total magnetic moments in the range of \( 3–50 \mu_B \), which have gain in binding energies as compared to the MES of a pure Mn13 cluster. Combining the results of Fig. 3 and Table I, it is therefore seen that the substitutional Ti doping as well as V doping of the Mn13 cluster are the most preferable in view of gaining significant amounts of both the binding energy and the total magnetic moment. For the MES of a Mn12Cr cluster, although the gain in magnetic moment is quite significant, the gain in binding energy is the least. Similarly, Mn12Fe, Mn12Co, and Mn12Ni clusters also have some isomers with total magnetic moments in the range of \( \sim 3–30 \mu_B \) [as seen from Fig. 3(b)], which have both gains in binding energy and magnetic moment with respect to those of the MES for a pure Mn13 cluster. However, the MESs for Mn12Fe, Mn12Co, and Mn12Ni clusters have total magnetic moments of 8\( \mu_B \), 7\( \mu_B \), and 8\( \mu_B \), respectively, which are higher than that of the MES for a Mn13 cluster, also, but significantly lower than that of the MESs for Mn12Ti and Mn12V clusters. In order to have a visual depiction of the trend in the choice of substituting elements in a concise manner, the binding energies and magnetic moments of the MESs of Mn12X clusters with respect to those of the MES with 0.5 electrons are plotted in Fig. 4.

In Fig. 5, we have plotted the total density of states and center-atoms projected density of states of the MES of each Mn12X cluster. As is seen from Fig. 5, the difference between the majority- and minority-spin states is large for the optimal icosahedral Mn12Ti, Mn12V, and Mn12Cr clusters, which results in large magnetic moments for these clusters. On the other hand, the magnetic moments for the optimal icosahedral structures of Mn13, Mn12Fe, Mn12Co, and Mn12Ni clusters are relatively small, as the majority- and minority-spin states mostly cancel each other out. Center-atoms projected density of states shows that it has a finite but small magnetic moment.

### Table I. Total binding energies and total magnetic moments (M) of the minimum energy icosahedral structures of Mn12X clusters, X = Ti, V, Cr, Mn, Fe, Co, Ni.

| Clusters | Binding energy (eV) | M (\( \mu_B \)) |
|----------|-------------------|---------------|
| Mn12Ti   | 29.812            | 30            |
| Mn12V    | 29.582            | 29            |
| Mn12Cr   | 28.122            | 22            |
| Mn12Fe   | 28.911            | 22            |
| Mn12Co   | 29.151            | 22            |
| Mn12Ni   | 29.062            | 8             |
| Mn13     | 28.023            | 3             |

FIG. 3. (Color online) Plot of total binding energies of icosahedral Mn12X clusters as a function of total magnetic moment (M). The total binding energies are plotted with respect to the binding energy of the MES of an icosahedral Mn13 cluster. (a) and (b) correspond to the substitutions by the elements to the left and to the right of Mn in the Periodic Table, respectively. The dotted lines through zero in (a) and (b) correspond to the binding energy of MES for a pure Mn13 cluster. The data points corresponding to the minimum energy structure of each Mn12X cluster are marked in the zoomed plots, shown as insets in (a) and (b).

FIG. 4. (a) Binding energies \( E_{diff} = E_B(Mn12X)_{MES} - E_B(Mn13)_{MES} \) and (b) magnetic moments \( M_{diff} = M(Mn12X)_{MES} - M(Mn13)_{MES} \) of the minimum energy structures of Mn12X clusters with respect to those of the minimum energy pure Mn13 cluster, respectively. The straight lines through zero in (a) and (b) are the reference fixed at the binding energy and total magnetic moment, respectively, of the MES of a pure Mn13 cluster.

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(0.1 eV) has been used.

the Fermi energy of that system. Gaussian smearing dotted line through zero parallel to the channel and dashed red curves for the minority-spin channel. The clusters. Black curves correspond to the results for the majority-spin panel) of the minimum energy icosahedral structures of Mn12X clusters. The consequences of these results have been discussed in detail in the following section.

D. Origin of stability and enhanced magnetism of the MESs of Mn12X clusters

To understand the relative stability of the doped Mn12X clusters, we have computed the binding energies of MnX dimers as given in Table II and also plotted the spin gaps [as defined in Eq. (2)] for the MESs of the Mn12X clusters in Fig. 6. Our calculated binding energies for dimers follow the same trend as we observed in case of clusters. It is seen from Table II that the MnTi dimer has a maximum binding energy of 3.14 eV.

Again, the binding energy of the MnV dimer (∼2.72 eV) is also quite high. Therefore, the large gains in binding energies of Mn12Ti and Mn12V clusters come from the large binding energies of MnTi and MnV dimers, respectively. On the other hand, the MnFe, MnCo, and MnNi dimers also have large binding energies as compared to those of the Mn2 dimer. Consequently, the Mn12Fe, Mn12Co, and Mn12Ni clusters also have larger binding energies as compared to the pure Mn13 cluster.

For comparison, we have also listed the previously calculated values of binding energies and bond lengths of the dimers as reported in Ref. 26. Our calculated values follow the similar trend as obtained from the reported values for both bond lengths and binding energies of the dimers. However, we note that the reported binding energies in Ref. 26 show the least value for the MnCr dimer and followed by the Mn2 dimer, while our calculated binding energies for dimers show the least value for the Mn2 dimer, followed by the MnCr dimer. In order to verify our calculation for the MnCr dimer, we have also performed the calculation for the Cr2 dimer. Our calculated binding energy and bond length for a Cr2 dimer are 2.08 eV and 1.59 Å, respectively. These values are consistent with the experimental values for a Cr2 dimer.27 Considering a mixed dimer with Mn and Cr, then the corresponding values for the MnCr dimer should be in between the corresponding values of the two pure dimers—Mn2 and Cr2. Our calculated values of binding energy and bond length for a MnCr dimer follow this trend. Both of the spin gaps (δ1 and δ2) as plotted in Fig. 6 are also positive for all the clusters studied here, indicating the formation of stable clusters. We find that the MESs of Mn12Ti and Mn12V clusters have large positive values of δ’s, which in turn, again indicate the high stability of the Mn12Ti and Mn12V clusters as compared to the others.

To understand the magnetic behavior of the MESs of the Mn12X clusters, we have calculated the atom-centered magnetic moments within a specified sphere around each atom of the MESs of doped Mn12X clusters and a pure Mn13 cluster. Figure 7 shows the pictorial representation of our analysis. Focusing first on the individual moments, we find that the moments of all the atoms for each cluster remain close to the atomic moment (∼3–4μB).

FIG. 5. (Color online) Plot of total density of states (left-hand panel) and center-atom projected total density of states (right-hand panel) of the minimum energy icosahedral structures of Mn12X clusters. Black curves correspond to the results for the majority-spin channel and dashed red curves for the minority-spin channel. The dotted line through zero parallel to the y axis in each system corresponds to the Fermi energy of that system. Gaussian smearing (0.1 eV) has been used.

in the case of MESs of Mn12Ti, Mn12V, and Mn12Cr clusters. On the other hand, its magnetic moment is remarkably small for the MESs of Mn13, Mn12Fe, Mn12Co, and Mn12Ni clusters. The consequences of these results have been discussed in detail in the following section.

| Dimers   | Binding energy (eV) | Bond length (Å) |
|----------|---------------------|-----------------|
| MnTi     | 3.14                | 1.80            |
| MnV      | 2.72                | 1.65            |
| MnCr     | 1.17                | 2.34            |
| Mn2      | 1.01                | 2.58            |
| MnFe     | 1.76                | 2.39            |
| MnCo     | 2.17                | 2.06            |
| MnNi     | 2.67                | 2.06            |

FIG. 6. Plot of spin gaps [as defined in Eq. (2)] of the MESs of Mn12X clusters.
highly coordinated central atom (atomic index 13), which has a small magnitude for all the Mn\(_{12}\)X clusters. It is therefore the alignment of individual moments of the surface atoms that plays a major role in determining the total magnetic moment of the MESs of the Mn\(_{12}\)X clusters. In the case of doping with an atom of the elements to the left of Mn in the Periodic Table (i.e., for the Mn\(_{12}\)Ti, Mn\(_{12}\)V, and Mn\(_{12}\)Cr clusters), it is seen that the surface Mn atoms are mostly ferromagnetically aligned. For example, only the moments of two surface atoms are antiferromagnetically aligned with the moments of other surface atoms, as in the case of MESs for Mn\(_{12}\)Ti and Mn\(_{12}\)V clusters. Similarly, the moments of three surface Mn atoms are antiferromagnetically aligned with the moments of other surface atoms, as in the case of the MES for a Mn\(_{12}\)Cr cluster. On the other hand, the surface Mn atoms are mostly antiferromagnetically coupled among themselves in the case of substitution with an atom of the elements to the right of Mn in the Periodic Table (i.e., for Mn\(_{12}\)Fe, Mn\(_{12}\)Co, and Mn\(_{12}\)Ni clusters) and the net magnetic moment for each of these clusters is small, close to the total magnetic moment of two ferromagnetically coupled Mn atoms, which is 10\(\mu_B\).\(^{10}\)

We further find that the magnetic moment of the central atom, although it is small as compared to that of the surface atoms for each doped cluster, varies from one doped cluster to another. It shows a systematic increase as one moves from Mn\(_{12}\)Ti \(\rightarrow\) Mn\(_{12}\)V \(\rightarrow\) Mn\(_{12}\)Cr and attains miniscule values for Mn\(_{13}\), Mn\(_{12}\)Fe, Mn\(_{12}\)Co, and Mn\(_{12}\)Ni. The moment at the central site is decided by two factors: (i) gradual filling of electronic states in moving from the left to the right of the Periodic Table and (ii) the hybridization with neighboring atoms. The gradual filling of electronic states should increase the moment in moving from Ti to V to Cr, attaining a maximum value for the half-filled case of Mn, followed by a gradual decrease in moving from Fe to Co to Ni. While the above-mentioned trend is observed for the central atom of Mn\(_{12}\)Ti, Mn\(_{12}\)V, and Mn\(_{12}\)Cr clusters, the moments for the central atom are all miniscule for Mn\(_{13}\), Mn\(_{12}\)Fe, Mn\(_{12}\)Co, and Mn\(_{12}\)Ni clusters, in contrast to the electron filling trend, which would demand the moment to be the maximum for Mn\(_{13}\). This is, however, explained by the second effect, namely, the hybridization effect. As the bond length decreases, generally the magnetic moment also decreases through an increase in effective hybridization. In order to examine the effect of hybridization, we have, therefore, calculated the center-to-surface average distance for the MESs of all the seven Mn\(_{12}\)X clusters with X = Ti, V, Cr, Mn, Fe, Co, Ni. Figure 8 shows the plot of our calculation. We find the average bond lengths to grow in moving from Mn\(_{12}\)Ti to Mn\(_{12}\)V to Mn\(_{12}\)Cr and then dropping suddenly to a smaller value for Mn\(_{13}\), which stays as a smaller value for Mn\(_{12}\)Fe, Mn\(_{12}\)Co, and Mn\(_{12}\)Ni clusters, also. The hybridization effect therefore takes over the filling effect in producing small magnetic moments at the central sites for Mn\(_{13}\) as well as for Mn\(_{12}\)Fe, Mn\(_{12}\)Co, and Mn\(_{12}\)Ni. Therefore, we find that the central atom behaves as a magnetic atom in the case for Mn\(_{12}\)Ti, Mn\(_{12}\)V, and Mn\(_{12}\)Cr clusters, while it behaves as essentially a nonmagnetic atom in case for Mn\(_{13}\), Mn\(_{12}\)Fe, Mn\(_{12}\)Co, and Mn\(_{12}\)Ni clusters. Considering the alignment of moments for both the surface atoms as well as the central atom, we can then conclude that when the central atom is magnetic, the surface Mn atoms are mostly antiferromagnetically coupled with the central atom, causing the effective ferromagnetic coupling among the surface atoms, which gives rise to a large total magnetic moment of the clusters. On the other hand, when the central atom is nonmagnetic, the surface magnetic moments interact with each other through a superexchange path involving the central nonmagnetic atom, resulting in antiferromagnetic coupling within each other. This gives rise to a small net magnetic moment of the whole clusters.

FIG. 7. (Color online) Individual atomic magnetic moments (\(m\)) of the MESs of Mn\(_{12}\)Ti, Mn\(_{12}\)V, Mn\(_{12}\)Cr, Mn\(_{13}\), Mn\(_{12}\)Fe, Mn\(_{12}\)Co, and Mn\(_{12}\)Ni clusters. The atomic indices 1–12 correspond to the surface atoms (the same for each Mn\(_{12}\)X cluster), while index 13 corresponds to the central atom, as shown in Fig. 2. Lengths of the bars correspond to the magnitude of atomic moments. Red colored (dark) bars in the positive direction correspond to \(+ve\) magnetic moments and green colored (gray) bars in the negative direction for \(-ve\) magnetic moments. The central site is the most coordinated site and therefore has a very small magnetic moment for all the clusters.

FIG. 8. Plot of center-to-surface average bond lengths (\(<r>\)) of the MESs of Mn\(_{12}\)X clusters.
The insets show the atomic spin orientation of the minimum energy structures of inset have a negative magnetic moment. The numbers in the parentheses for the insets correspond to the total magnetic moment and the relative energy to the MES of the Mn13N cluster, respectively.

**E. N-capped Mn13N cluster**

Finally, in order to see the effect of N capping in a Mn13 cluster along the same direction as discussed in Ref. 12, we have also studied the structure, stability, and magnetic properties of an icosahedral Mn13N cluster with the N atom as a triangular face cap as shown in the inset of Fig. 9. To determine the magnetic moment of the MES and to identify the possible isomers close to MES, we have again optimized the structure for all possible collinear spin configurations of atoms. We find an icosahedral structure of a total magnetic moment of 12μB is the MES for the Mn13N cluster. We also find that the Mn-N-Mn bond angles of the N atom with the three nearest Mn atoms, in the case of the MES of Mn13N cluster, are 90.08°, 93.95°, and 90.97°. This nearly 90° bond angle between Mn-N-Mn has been predicted as the guiding rule for the ground-state structure of N-capped Mn clusters in earlier work.12 It results from the interaction of the p orbitals of the N atom with the s-d hybridized orbitals of Mn atoms. As the N atom is added, the binding energy of the Mn13N cluster improves significantly as compared to that of the MES for the pure Mn13 cluster. The energy gained in adding a N atom to a Mn13 cluster is defined as

$$\Delta = -[E(\text{Mn13N}) - E(\text{Mn13}) - E(N)]$$

Figure 9 shows the variation of Δ as a function of total magnetic moment of the Mn13N cluster. The MES of the Mn13N cluster has a binding energy gain Δ = 6.42 eV. There are also several closely lying isomers with total magnetic moments of 22μB, 10μB, and 2μB, which are 4, 10, and 14 meV away from that of the MES, respectively. So the Δ’s for them are also very close to that of the MES. These values of Δ’s are consistent with the energy gain predicted in Ref. 12 for the Mn13 cluster, which is 5.61 eV. In the earlier work,12 it has been shown that the addition of one N atom to at least five Mn atoms is energetically favorable. Here we see that the addition of a single N atom is also energetically favorable even for the Mn13 cluster. This enhancement in bonding owing to N addition has been demonstrated earlier12 by examining the bonding in the case of a dimer Mn2 vs Mn2N. The lack of hybridization between the s and d electrons owing to a filled 4s shell of Mn prevents Mn2 from forming a strong bond. As N is attached, the 4s2 electrons of Mn interact with the 2p3 electrons of N, resulting in strong coupling. The inset of Fig. 9 shows the orientations of atomic spins of the minimum energy structure of magnetic moment 12μB and the first isomer of magnetic moment 22μB of the Mn13N cluster. The local effect of N capping is now very obvious. Effectively, it couples the atomic spins ferromagnetically in the triangular face, where it sits as well as in the pentagonal ring nearest to it (upper pentagonal rings of the two structures in the insets of Fig. 9). Therefore, two pentagons for each of the two structures (MES and the closely lying first isomer) in the inset of Fig. 9 are now effectively ferromagnetically coupled. So, in addition to enhancing binding, N capping also increases the magnetic moment as compared to that of the pure Mn13 cluster. However, it is significantly lower than that of the MESs for Mn12Ti and Mn12V clusters, presumably owing to the fact that N capping produces a local effect while the Ti or V substitutions at the central site effects all of the other 12 surface atoms, thereby producing a global effect.

**IV. SUMMARY AND CONCLUSIONS**

The total magnetic moment of a Mn13 cluster is small owing to antiferromagnetic alignment of individual atomic moments. Our study shows that it is possible to obtain a stable ferromagnetic alignment of atomic spins by substitutional Ti doping and V doping in a Mn13 cluster, resulting into giant total magnetic moment. We have compared our findings with the previously proposed route of N capping to Mn clusters. The gain in magnetic moment compared to a pure Mn13 cluster is found to be more in the case of Ti and V substitutions. Also, substitutional doping keeps the volume of the parent cluster intact, while the N capping increases the effective volume of the cluster. Therefore, we propose Ti substitution and V substitution as promising alternatives to engineer the magnetic structure for a Mn13 cluster.

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