First principles study of Sc, Ti and V doped Naₙ (n = 4, 5, 6) clusters: Enhanced magnetic moments

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Theoretical studies on the geometry, electronic structure and spin multiplicity of Sc, Ti and V doped Naₙ (n = 4, 5, 6) clusters have been carried out within a gradient corrected density functional approach. Two complementary approaches including all-electron calculations on free clusters, and supercell calculations using plane wave pseudopotential and projector augmented wave formalisms have been carried out. It is shown that spin magnetic moments of the transition metal atoms, the magnitude of host polarization, and the sign of the host polarization all change with the number of alkali atoms. In particular the transition metal atoms are shown to attain spin moments that are higher than their atomic values. The role of hybridization between the transition atom d-states and the alkali sp-states is highlighted to account for the evolutions in the spin moments and host polarization.

I. INTRODUCTION

Extensive research over the past two decades has shown that atomic clusters consisting of two to a few hundred atoms constitute a new phase of matter with distinct properties different from those of individual atoms on the one hand and bulk matter on the other. Of all the properties, the magnetic properties in reduced sizes are probably the most fascinating. Small clusters of itinerant ferromagnetic solids Fe, Co, and Ni are found to possess enhanced magnetic moments that can be around 30% higher than the bulk moments. These clusters also exhibit super paramagnetic behavior as a consequence of reduced magnetic anisotropy as opposed to the ferromagnetic behavior observed in solids. Small clusters of non-magnetic solids like Rh are found to be magnetic with appreciable moments per atom that disappear as the size approaches around 100 atoms. Transition metal (TM) atoms doped in clusters of other metals also show very interesting magnetic properties. Recently, Li et al. studied 3d TM doped Au₆ clusters both experimentally, and theoretically through density functional theory (DFT) calculations. In these clusters, the TM atoms were found to retain their atomic moments. Later, Torres et al. reported DFT calculations of TM doped small cationic Au clusters in which the magnetic moment showed pronounced odd-even effects as a function of the cluster size, and resulted in values very sensitive to the geometrical environment. In all these cases, the moment per atom in the clusters are less than or equal to the possible spin magnetic moment in the individual atom. It has however been recently reported that atomic and even magnetic moments beyond the atomic value on transition metal atoms can be stabilized by depositing them on alkali metal surfaces and in the interior of alkali hosts. For example, Bergmann and Song have carried out anomalous Hall effect measurements on systems consisting of Vanadium impurities on Na and K thin films. Vanadium is non-magnetic in the solid phase. Yet, the measurements by Bergman and Song indicate a large moment in the range of 6.6 to 7 µB per atom. Sahu and Kleinman have carried out first principles theoretical studies on Vanadium inside alkali hosts using a supercell approach. The theoretical studies suggest that the absolute value of the moment may be less than that predicted by Bergman and Song. Both studies, however, do confirm large spin moments on V sites indicating that alkali hosts can stabilize and enhance spin moments on transition metal sites.

In this paper, we present an intriguing finding where the spin magnetic moment of transition metal atom and the polarizability of the host atoms can be controlled by changing the size of the alkali host. Our investigations cover Sc, Ti, and V atoms deposited on alkali templates consisting of four, five and six sodium atoms. The investigations employ first principles theoretical studies within a gradient corrected density functional to incorporate the exchange and correlation effects. We demonstrate that as the cluster size is changed, the three impurities exhibit differing behavior. While the spin moment of Sc and V atoms oscillate as the number of alkali atoms is changed, the moment of Ti atom monotonically increases as the size is increased. A detailed analysis of the atomic spin charges on Na atoms shows that while the host polarization enhances the spin moment in some cases, it opposes that in others. The ability to control the spin moment and the host polarization by changing the metal atom and the size of the alkali
cluster offers unique opportunities for tuning magnetic moment and coupling in such systems.

## II. COMPUTATIONAL METHODS

All the theoretical studies were carried out within the gradient corrected DFT framework. We carried out all-electron calculations with atom-centered Gaussian type orbitals using the deMon2K code\(^\text{18}\). These calculations employed the PW86 generalized gradient approximation (GGA) functional\(^\text{19}\), and the DZVP basis sets optimized for gradient corrected exchange-correlation functionals\(^\text{20}\). In order to avoid the calculation of four-center electron repulsion integrals, the variational fitting of the Coulomb potential\(^\text{21,22}\) was employed. The auxiliary density was expanded in primitive Hermite Gaussian functions using the A2 auxiliary function set\(^\text{23}\). The exchange-correlation potential was calculated with the orbital density. Structures were optimized using the quasi-Newton method in internal redundant coordinates\(^\text{24}\) for different fixed spin multiplicities, and without any symmetry constraints. Supplementary calculations were performed in order to eliminate any uncertainty due to the basis set or the numerical procedure. We also carried out plane-wave pseudopotential calculations using a supercell approach. Here, an energy cutoff of 500 eV was used, and the cluster was placed in a large cubic box of sides 20 Å in order to reduce its interaction with its images. The potential between the ion cores and the valence electrons were expressed in terms of the Vanderbilt-type ultra-soft pseudopotential (USPP)\(^\text{25}\). The exchange-correlation effects were treated with the PW91\(^\text{26}\) GGA functional. Brillouin zone integrations were carried out using only the Γ-point. Structures were relaxed using the conjugate gradient (CG) method for different fixed spin multiplicities, and without any symmetry constraints. We re-calculate total energies of all clusters using projector augmented wave (PAW) method in the same geometry as obtained from USPP calculations. These calculations were carried out using VASP code\(^\text{27,28,29}\). It turned out that the all-electron, USPP and PAW calculations all agreed on the lowest energy spin multiplicity for each cluster. We found some differences in the energy orderings and spin multiplicities of excited states between the plane-wave and Gaussian type methods; however these differences are small in most of the cases. In what follows we report the geometries and energy values based on all-electron deMon2K calculations, unless otherwise mentioned.

## III. RESULTS AND DISCUSSION

### A. Pure Na clusters

In order to benchmark our calculations, we first calculated structures and binding energies (BE) of pure Na\(_n\) clusters in the size range \(n = 3, 4, \ldots, 10\) where previous calculations exist. Binding energy of a cluster is defined as the energy gain in assembling the cluster from the isolated atoms. For pure Na clusters this is given by the equation:

\[
BE(\text{Na}_n) = nE(\text{Na}) - E(\text{Na}_n),
\]

where \(E(\text{Na}_n)\) represents the total energy of a Na\(_n\) cluster, and \(E(\text{Na})\) is the total energy of an isolated Na atom. Note that according to this definition, BE is a positive number for a bound structure, and a larger BE implies a more stable structure.

In both all-electron and USPP methods we were able to reproduce the previously reported structures of pure Na clusters\(^\text{30}\). In particular, we reproduced the \(C_{2v}\) structure for a pure Na\(_5\) cluster, and for a Na\(_6\) cluster we found two close lying isomers with \(C_{5v}\) and \(D_{3h}\) symmetries. We found the 3-dimensional (3D) \(C_{5v}\) structure to be marginally (~ 0.03 eV) lower in energy than the planar \(D_{3h}\) structure. Earlier calculations\(^\text{30,31}\) also found these two structures to be very close in energy with different methods giving different energy ordering. We also found that the BE per Na atom shows a peak at \(n = 8\) relative to neighboring sizes. Enhanced stability of Na\(_8\) with 8 valence electrons has been previously rationalized within a jellium model\(^\text{32}\) where the cluster corresponds to a magic species with filled electronic shell.

Having confirmed that our calculations reproduce the known structures and energetics of pure Na clusters at small sizes correctly, we then studied TM doping in Na\(_n\) clusters for \(n = 4 - 6\). At each size, we tried several initial geometries and relaxed them for different fixed spin states without any symmetry constraints. We now discuss the results of these calculations. Figure \[\text{Figure}\] presents the optimized geometries and Mulliken atomic spin charges of the ground state and the next higher lying isomer in energy for the series TMNa\(_n\) \((n = 4, 5, \text{and } 6 \text{ and TM } = \text{Sc, Ti, and V})\), and in Table \[\text{Table}\] we present the magnetic moment and relative energies of these clusters.
B. TMNa$_4$ clusters

In the case of TMNa$_4$ clusters, we found two low lying structures for ScNa$_4$ which are shown in Figure 1. We found the same structure for the ground state for ScNa$_4$, TiNa$_4$ and VNa$_4$ clusters. This structure is obtained by replacing the Na atom with the highest coordination number in the C$_{2v}$ structure of a pure Na$_4$ cluster by a TM atom. ScNa$_4$ and TiNa$_4$ clusters retain the atomic moments of the Sc and Ti atoms, 1 and 2 $\mu_B$ respectively. What is intriguing and amazing is that the VNa$_4$ cluster has an enhanced magnetic moment of 5 $\mu_B$, while that of a V atom in the ground state is only 3 $\mu_B$. The microscopic reason behind this enhanced magnetic moment is discussed later.

A summary of the results on these clusters are presented in Table I. It is to be noted, however, that both for TiNa$_4$ and VNa$_4$ clusters, the high and low spin-multiplicity states are very close in energy, while the two structural isomers of ScNa$_4$ are also close in energy.

C. TMNa$_5$ clusters

For TMNa$_5$ clusters, the low energy structures we found are: (i) a C$_{5v}$ structure with a TM atom incorporated at the center of a Na$_5$ pentagon for the ground states of TiNa$_5$ and VNa$_5$; (ii) a square bipyramidal structure having C$_{4v}$ symmetry for the ground state of ScNa$_5$ and the low lying isomer of VNa$_5$ and, (iii) a structure with C$_v$ symmetry that is obtained by distorting the C$_{4v}$ structure for the low lying isomers of ScNa$_5$ and TiNa$_5$. These structures are shown in Figure 1 and the main results of our calculations for TMNa$_5$ clusters are presented in Table II.

Although the ScNa$_5$ cluster has no net moment in its lowest energy structure, we found a nearly isoeenergetic state with magnetic moment of 2 $\mu_B$ only 0.003 eV higher in energy. TiNa$_5$ and VNa$_5$ clusters presented large moments of 3 and 4 $\mu_B$ respectively in their ground states. The next higher energy structures/multiplets of TiNa$_5$ and VNa$_5$ are separated by significant energy differences 0.1 eV and 0.3 eV respectively from the ground states. As we discuss below, similar large moments are found in Ti and V doped Na$_6$ clusters and such large magnetic moments seem to be a feature of early TM doped small Na clusters.

D. TMNa$_6$ clusters

For TMNa$_6$ clusters, we studied both planar and 3D structures having various symmetries within plane-wave USPP and PAW methods. In a planar geometry, we placed the TM at the center of a Na$_6$ hexagon. In this geometry, ScNa$_6$ has a moment of 3 $\mu_B$, while the Ti and V doped clusters have moments as large as 4 $\mu_B$ and 5 $\mu_B$ respectively.

As for 3D structures for TMNa$_6$ clusters, we found stable structures with C$_{5v}$, and C$_{3v}$ or C$_s$ symmetries as shown in Figure 1. In all the cases, the C$_{5v}$ structure turned out to be the ground state. This pentagonal bipyramid structure is exactly what was found for the MgNa$_6$ cluster and is also equivalent to attaching a TM atom to the C$_{5v}$ structure for a pure Na$_6$ cluster.

The 3D structures turned out to be significantly more favorable in energy than the planar structure. The ground states of ScNa$_6$, TiNa$_6$ and VNa$_6$ present moments of 1, 4 and 5 $\mu_B$ respectively. The next higher energy low lying isomers of TiNa$_6$ and VNa$_6$ have magnetic moments of 2 and 3 $\mu_B$, which are separated from the ground states by 0.03 eV and 0.13 eV respectively. These results are presented in Table II. Li et al. have claimed that Ti and V doped Au$_6$ clusters have moments of 2 and 3 $\mu_B$ respectively. Here we find that Ti and V doped Na$_6$ clusters posses even larger moments. In case of V our results agree with the experimental study of Bergmann et al. that predict a high magnetic moment of 6-7 $\mu_B$ for V as an impurity in bulk Na. These results, we believe, can provide an important way to produce magnetic clusters with large moments. In order to convince ourselves that the large magnetic moments we found on these clusters were not artifacts of the methods we used, and to further benchmark our calculations, we also calculated the properties of a CrAu$_6$ cluster in a planar geometry using plane-wave USPP method for which previous studies exist.

In agreement with Li et al., we obtained a moment of 4 $\mu_B$. The molecular orbitals (MO) diagram we found was in very good agreement with that presented in Fig. 3 of ref. 13.

One of the important questions is the nature of the polarization at the alkali metal sites. When a transition metal atom is embedded in a bulk free electron host, it is known that a many body state where the host polarization is opposed to the transition metal moment can be formed. This leads to the well known Kondo resonance. It is then interesting to ask how such an effect is modified in reduced sizes. In Figure 2 we give the spin moment on the atoms obtained by carrying out a Mulliken population analysis of the atomic spin charges. Note that the host polarization changes in magnitude and sign as the cluster size is changed. These modifications can be linked to the location of the electronic states and their interactions between the host and the transition metal that we discuss below.

We now try to understand the origin of such larger-than-atom magnetic moments in these clusters and the nature of the host polarization. Figure 2 shows the MO diagram for Na$_4$, TMNa$_4$ and TM atoms. The angular momentum
characters of the MO’s are also presented. Not surprisingly, more type MO’s get occupied as the TM atom is changed from Sc to V. For ScNa$_4$ in the majority $\alpha$ spin channel, we found that the highest occupied molecular orbital (HOMO), and HOMO-1 have largely $d$ character on the Sc atom, along with some $s$ and/or $p$ contributions from the Na atoms ($s,p_{Na}$ $d_{Sc}$ in our nomenclature). In the minority $\beta$ spin channel, the HOMO level is a mix of $s$ and $p$ type orbitals on Na ($s,p_{Na}$), and $p$ type orbitals on Sc ($p_{Sc}$). The lowest unoccupied MO’s (LUMO’s) in the $\alpha$ and $\beta$ spin channels are of $s,p_{Na}$ $d_{Sc}$ type. In TiNa$_4$ we found that the HOMO and HOMO-2 levels presented a $s,p_{Na}$ $d_{Ti}$ character and that HOMO-3 is mainly of $d_{Ti}$ character. VNa$_4$ is the first cluster to exhibit an enhanced magnetic moment. An analysis of the MO characters shows that the HOMO and HOMO-2 levels presented a $s,p_{Na}$ $d_{V}$ character. HOMO-3 and HOMO-5 are of $d_{V}$ character. We can observe that in the ScNa$_4$, TiNa$_4$ and VNa$_4$ series the spd hybridization increases, as there is an increasing number of $d$ levels available at lower energies in the Sc, Ti and V series.

Figure 3 shows the MO diagram for Na$_5$, TMNa$_5$ and TM atoms. In this series the TiNa$_5$, VNa$_5$ clusters presented enhanced magnetic moments. An analysis of the character of the MO’s shows a spd hybridization ($s,p_{Na}$ $d_{Sc}$) in the case of ScNa$_5$. Interestingly, the MO’s of TiNa$_5$ and VNa$_5$ present a $s,p_{Na}$ $p_{TM}$ (and not $s,p_{Na}$ $d_{TM}$) character. In TiNa$_5$ we found that the doubly degenerate HOMO, and the HOMO-1 levels are mainly of $d$ character. This result shows that in addition to hybridization there is a charge transfer from the Na $s$ levels to the Ti $d$ states, as an isolated Ti atom possesses only two filled $d$ states. The same picture was found in VNa$_5$ where the degenerated HOMO and HOMO-2 levels are of $d$ character. Figure 4 shows the MO diagram for Na$_6$, TMNa$_6$ and TM atoms. In this series also the clusters with Ti and V presented enhanced magnetic moments. Analysis of the MO’s characters suggests an spd hybridization to be responsible for this enhancement.

We conjecture that the major reason for the enhanced magnetic moments on these clusters is this significant spd hybridization. In fact, total occupancy of $d$ and spd states in some of these clusters is larger than the occupancy of $d$ states in the respective isolated TM atoms. Normally hybridization of atomic orbitals leads to quenching of atomic moments. Here, hybridization along with a large exchange splitting has an opposite effect. For example, exchange splitting (defined as the energy difference between the highest $\alpha$-spin MO and the lowest $\beta$-spin MO having predominantly $d$ characters) in TiNa$_6$ and VNa$_6$ clusters is $\sim 1$ and $\sim 1.8$ eV respectively.

A comparison of the TM doped Na$_6$ clusters with the TM doped Au$_6$ clusters reported by Li et al.\cite{13} is of some importance here. In the Au$_6$ cluster, the TM’s act like guest atoms. The spectral features of the TMAu$_6$ clusters showed two distinct regions which could be attributed to a TM atom and to an Au$_6$ ring. This conclusion was borne out by their DFT calculations which revealed that the MO’s near the gap were mostly of pure $d$-type on the TM atom, and there was a substantial gap between these levels and the deeper lying levels derived from the Au$_6$ hexagon. In the present study there is no clear guest-host separation of MO’s in TMNa$_n$ clusters. On the contrary, in TiNa$_n$ and VNa$_n$ clusters, at least part of the moment comes from states that have significant spd mixing as we have argued.

Relative values of electronegativity of Na and TM atoms may also have a crucial role to play. Na has a smaller (Pauling) electronegativity compared to the TM atoms. Thus, nominally one expects charge transfer from the Na to the TM atoms. This explains the charge transfer found in the TMNa$_5$ clusters. In contrast to Na, Au has a (Pauling) electronegativity value much larger than those of Ti, V and Cr, suggesting that there should be a charge transfer from TM atoms to Au. Indeed, Torres et al.\cite{14} found in their DFT calculations that the charge transfer from TM to Au atoms in TMAu$_n^+$ clusters roughly follows the sequence of electronegativity difference between Au and TM atoms, and for small cluster sizes the Au-TM bond is mainly ionic. The amount of charge transfer from the TM to the Au atoms determines the moment on the TM atom. In TMNa$_n$ clusters, as we have already shown, overlap of Na $s$ and $p$ and TM $d$ type orbitals increases the moment on the TM atoms.

The relative stability of a TMNa$_n$ clusters can be measured by the embedding energy (EE) of the TM in the Na$_n$ cluster. This is defined as,

$$EE(TMNa_n) = E(Na_n) + E(TM) - E(TMNa_n),$$

where $E(TMNa_n)$ is the ground state total energy of a TM doped Na$_n$ cluster, $E(Na_n)$ is the total energy of a pure Na$_n$ cluster, and $E(TM)$ is the total energy of an isolated TM atom. It has been shown before that it is important to preserve spin multiplicity while calculating embedding energies.\cite{25,26} Therefore, in calculating EE we used total energies of excited states for TM and Na$_n$ when the spin multiplicities of the ground states did not satisfy the Wigner-Wittmer spin conservation rule.\cite{26} In calculating the EE for ScNa$_n$, TiNa$_4$, TiNa$_5$, and VNa$_5$ the ground state energies were employed. In the rest of the cases, excited states of either Na$_n$ cluster or the TM atom has been considered, whichever gives a larger EE. The calculated EE for the TMNa$_n$ series are presented in Table I.

It is interesting to note certain trends in this family of clusters. For each size from Na$_3$ to Na$_8$, EE increases as the TM atom is changed from Sc to Ti and V. For any given TM atom, the EE increases from Na$_4$ to Na$_5$ and Na$_6$. The second fact suggests that in experiments, these small clusters will tend to bind with other Na atoms and form larger clusters. Therefore, a study extending up to larger TMNa$_n$ clusters is of importance, and that is currently underway. A crucial question is, up to what size of Na clusters such large moments survive or how the moment evolves for a
given TM atom, as the number of Na atoms increases. This study will allow us to find out if Na clusters are able to present large magnetic moments in the range of 6.6 to 7 $\mu_B$ as found in the experimental studies of Bergmann et al.\textsuperscript{15,16}. Our preliminary calculations show that large moments survive on the Ti and V doped Na$_n$ clusters at least up to $n = 9$\textsuperscript{37}.

In order for any cluster to be technologically useful, it has to be chemically inert. One indication of chemical inertness is the gap between the HOMO and LUMO levels. HOMO-LUMO gaps for these clusters are shown in Table\textsuperscript{[8]. All the clusters have a large gap of $\sim 0.5$ eV or more. Some of them, in fact, have gaps in excess of 1 eV. The large EE values and HOMO-LUMO gaps are indicative of stability in these clusters, and reinforce the idea that they may have useful applications.

### IV. CONCLUSION

The present studies show that the size and structure of alkali metal clusters can significantly affect the spin magnetic moments of doped transition metal atoms. In particular, V doped Na$_4$, and Ti and V doped Na$_5$ and Na$_6$ clusters are shown to exhibit enhanced magnetic moments. ScNa$_6$ cluster also has a large moment of 3 $\mu_B$ in a low lying isoenergetic state. An analysis of the MO’s of TMNa$_n$ clusters suggests that a significant hybridization between Na $s$ and $p$ and TM $d$ type orbitals coupled with a large exchange splitting of $d$ type states, and a smaller value of electronegativity of Na compared to those of the TM atoms are responsible for the observed large moments and the host polarization. This conjecture is consistent with earlier calculations on neutral and cationic TMAu$_6$ clusters. We would like to add that the host polarization can be expected to stabilize the orientation of the transition metal moment providing spin anisotropy with respect to the geometry of the alkali host. These effects are being investigated.

### V. ACKNOWLEDGMENTS

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TABLE I: Electronic properties of the TMNaₙ clusters. Magnetic moments (µ), HOMO-LUMO gaps (Gap), and the embedding energies (EE) in the ground state. Magnetic moment in the low-lying isomer, and the energy difference with respect to the ground state (∆E).

| Cluster | Ground state | Low-lying isomer |
|---------|--------------|------------------|
|         | µ(µB) | Gap (eV) | EE (eV) | µ(µB) | ∆E (eV) |
| ScNa₄   | 1     | 0.65   | 1.10    | 1     | 0.025   |
| TiNa₄   | 2     | 1.03   | 1.17    | 4     | 0.013   |
| VN₄     | 5     | 0.41   | 1.73    | 3     | 0.064   |
| ScNa₅   | 0     | 0.51   | 1.32    | 2     | 0.030   |
| TiNa₅   | 3     | 0.92   | 1.50    | 3     | 0.104   |
| VN₅     | 4     | 1.17   | 1.89    | 4     | 0.283   |
| ScNa₆   | 1     | 0.67   | 1.56    | 1     | 0.076   |
| TiNa₆   | 4     | 0.48   | 1.89    | 2     | 0.030   |
| VN₆     | 5     | 0.68   | 2.21    | 3     | 0.128   |

Figure Captions

FIG. 1: (Color online) Ground state geometries (GS), and immediate higher energy isomers (EX) of the TMNaₙ clusters. The bond lengths are given in Angstroms and superscripts indicate spin multiplicity. The Mulliken atomic spin charges for the symmetry inequivalent atoms are marked below them.

FIG. 2: One-electron levels in Na₄, ScNa₄, Sc, TiNa₄, Ti, VN₄ and V, superscripts indicate the spin multiplicity. The continuous lines represent occupied levels; the dotted lines correspond to unfilled states. The degeneracy is marked by a number next to the level. The angular characters of the energy levels are also given. The arrows indicate the majority (up), and minority (down) spin states.
FIG. 3: One-electron levels in Na$_5$, ScNa$_5$, Sc, TiNa$_5$, Ti, VNa$_5$ and V, superscripts indicate the spin multiplicity. The continuous lines represent occupied levels; the dotted lines correspond to unfilled states. The degeneracy is marked by a number next to the level. The angular character of the energy levels is also given. The arrows indicate the majority (up), and minority (down) spin states.

FIG. 4: One-electron levels in Na$_6$, ScNa$_6$, Sc, TiNa$_6$, Ti, VNa$_6$ and V superscripts indicate the spin multiplicity. The continuous lines represent occupied levels; the dotted lines correspond to unfilled states. The degeneracy is marked by a number next to the level. The angular character of the energy levels is also given. The arrows indicate the majority (up), and minority (down) spin states.
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