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

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Theoretical studies on the geometry, electronic structure, and spin multiplicity of Sc, Ti, and V doped Na_n ($n=4,5,6$) 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.

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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.[1–6] Of all the properties, the magnetic properties in reduced sizes are probably the most fascinating.[7] 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.[8] These clusters also exhibit a superparamagnetic behavior as a consequence of reduced magnetic anisotropy as opposed to the ferromagnetic behavior observed in solids.[8–10] Small clusters of nonmagnetic solids such as Rh are found to be magnetic with appreciable moments per atom that disappear as the size approaches around 100 atoms.[11,12] Transition metal (TM) atoms doped in clusters of other metals also show very interesting magnetic properties. Recently, Li *et al.*[13] studied 3*d* TM doped Au_6 clusters both experimentally and theoretically through density functional theory (DFT) calculations. In these clusters, the TM atoms were found to retain their atomic moments. Earlier, Torres *et al.*[14] 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 is 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[15,16] have carried out anomalous Hall effect measurements on systems consisting of vanadium impurities on Na and K thin films. Vanadium is nonmagnetic in the solid phase. Yet, the measurements by Bergman and Song indicate a large moment in the range of 6.6–7 μ_B per atom. Sahu and Kleinman[17] 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 moments 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.[18] These calculations employed the PW86 generalized gradient approximation (GGA) functional[19] and the double zeta valence plus polarization (DZVP) basis sets optimized for gradient corrected exchange-correlation functionals.[20] In order to avoid the calculation of four-center electron repulsion integrals, the variational fitting of the Coulomb potential[21,22] was employed. The auxiliary density was expanded in primitive Hermite-Gaussian functions using the A2 auxiliary function set.[23] The exchange-correlation potential was calculated with the orbital density. Structures were optimized using the quasi-Newton method in internal redundant coordinates[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 of 20 Å in order to reduce its interaction with its images. The potential between the ion cores and the valence electrons was expressed in terms of the Vanderbilt-type ultrasoft pseudopotential (USPP).[25] The exchange-correlation effects were treated with the PW91[26] GGA functional. Brillouin zone integrations were carried out using only the Γ point. Structures were relaxed using the conjugate gradient method for different fixed spin multiplicities and without any symmetry constraints. We recalculate total energies of all clusters using the projector augmented wave (PAW) method in the same geometry, as obtained from USPP calculations. These calculations were carried out using the VASP code.[27–29] 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 (BEs) 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

$$\mathrm{BE}(\mathrm{Na}_n) = nE(\mathrm{Na}) - E(\mathrm{Na}_n), \tag{1}$$

where $E(\mathrm{Na}_n)$ represents the total energy of a Na_n cluster and $E(\mathrm{Na})$ 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.[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 three-dimensional (3D) C_{5v} structure to be marginally ($\sim$0.03 eV) lower in energy than the planar D_{3h} structure. Earlier calculations[30,31] also found these two structures to be very close in energy with different methods giving different energy orderings. 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 eight valence electrons has been previously rationalized within a jellium model[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 1 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, and 6 and TM=Sc, Ti, and V); in Table I, 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 Fig. 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_5 cluster by a TM atom. $ScNa_4$ and $TiNa_4$ clusters retain the atomic moments of the Sc and Ti atoms, 1 and 2 μ_B, respectively. What is intriguing and amazing is that the VNa_4 cluster has an enhanced magnetic moment of 5 μ_B, while that of a V atom in the ground state is only 3 μ_B. The microscopic reason behind this enhanced magnetic moment will be 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 (iii) a structure with C_s symmetry that is obtained by distorting the C_{4v} structure for the low lying isomers of $ScNa_5$, $TiNa_5$, and VNa_5. These structures are shown in Fig. 1 and the main results of our calculations for $TMNa_5$ clusters are presented in Table I.

Although the $ScNa_5$ cluster has no net moment in its lowest energy structure, we found a nearly isoenergetic state with a magnetic moment of 2 μ_B only 0.003 eV higher in energy. $TiNa_5$ and VNa_5 clusters presented large moments of 3 and 4 μ_B, respectively, in their ground states. The next higher energy structures and/or multiplets of $TiNa_5$ and VNa_5 are separated by significant energy differences of 0.1 and 0.3 eV, respectively, from the ground states. As we will discuss below, similar large moments are found in Ti and V

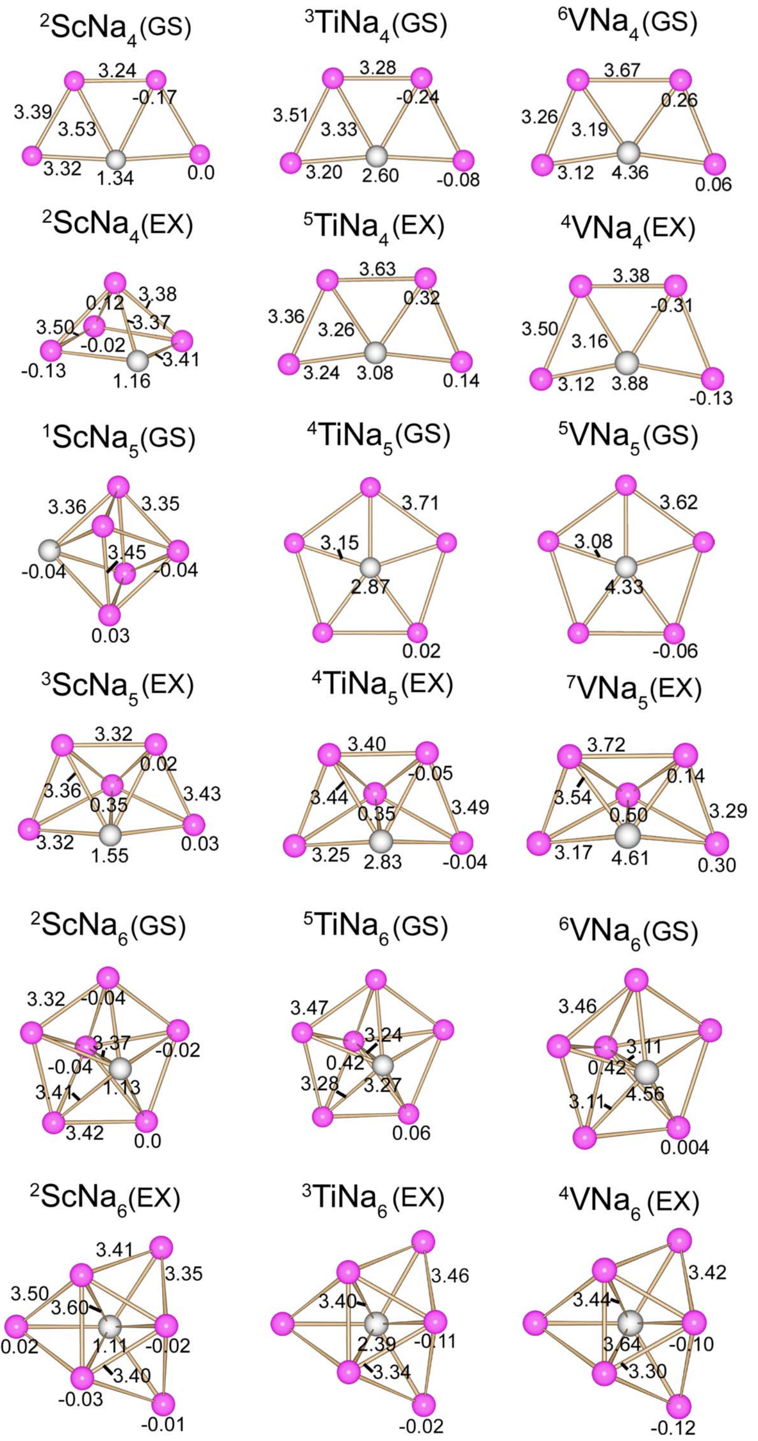

FIG. 1. (Color online) Ground state geometries (GS) and immediate higher energy isomers (EX) of the TMNa_n clusters. The bond lengths are given in angstroms and superscripts indicate spin multiplicity. The Mulliken atomic spin charges for the symmetry inequivalent atoms are marked below them.

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 μ_B, while the Ti and V doped clusters have moments as large as 4 and 5 μ_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 Fig. 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[33] 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

TABLE I. Electronic properties of the TMNa$_n$ 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 (ΔE).

	Ground state			Low-lying isomer	
Cluster	μ (μ_B)	Gap (eV)	EE (eV)	μ (μ_B)	ΔE (eV)
$ScNa_4$	1	0.65	1.10	1	0.025
$TiNa_4$	2	1.03	1.17	4	0.013
VNa_4	5	0.41	1.73	3	0.064
$ScNa_5$	0	0.51	1.32	2	0.003
$TiNa_5$	3	0.92	1.50	3	0.104
VNa_5	4	1.17	1.89	6	0.283
$ScNa_6$	1	0.67	1.56	1	0.076
$TiNa_6$	4	0.48	1.89	2	0.030
VNa_6	5	0.68	2.21	3	0.128

of $ScNa_6$, $TiNa_6$, and VNa_6 present moments of 1, 4, and 5 μ_B, respectively. The next higher energy low lying isomers of $TiNa_6$ and VNa_6 have magnetic moments of 2 and 3 μ_B, which are separated from the ground states by 0.03 and 0.13 eV, respectively. These results are presented in Table I. Li *et al.*[13] have claimed that Ti and V doped Au_6 clusters have moments of 2 and 3 μ_B, respectively. Here, we found that Ti and V doped Na clusters possess even larger moments. In the case of V, our results agree with the experimental study of Bergmann and Song[15,16] that predict a high magnetic moment of 6–7 μ_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.*,[13] we obtained a moment of 4 μ_B. The molecular orbital (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.[34] It is then interesting to ask how such an effect is modified in reduced sizes. In Fig. 1, 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 will 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 MOs are also presented. Not surprisingly, more d-type MOs get occupied as the TM atom is changed from Sc to V. For $ScNa_4$ in the majority α spin channel, we found that the highest occupied molecular orbital (HOMO) and HOMO-1 have a largely d character on the Sc atom, along with some s and/or p contributions from the Na atoms ($s,p_{\mathrm{Na}}d_{\mathrm{Sc}}$ in our nomenclature). In the minority β 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 MOs (LUMOs) in the α and β spin channels are of $s,p_{\mathrm{Na}}d_{\mathrm{Sc}}$ type. In $TiNa_4$, we found that the HOMO and HOMO-2 levels presented an $s,p_{\mathrm{Na}}d_{\mathrm{Ti}}$ 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 an $s,p_{\mathrm{Na}}d_{\mathrm{V}}$ 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 $TiNa_5$ and VNa_5 clusters presented enhanced magnetic moments. An analysis of the character of the MOs shows an *spd* hybridization ($s,p_{\mathrm{Na}}d_{\mathrm{Sc}}$) in the case of $ScNa_5$. Interestingly, the MOs of $TiNa_5$ and VNa_5 present an $s,p_{\mathrm{Na}}p_{\mathrm{TM}}$ (and not $s,p_{\mathrm{Na}}d_{\mathrm{TM}}$) 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

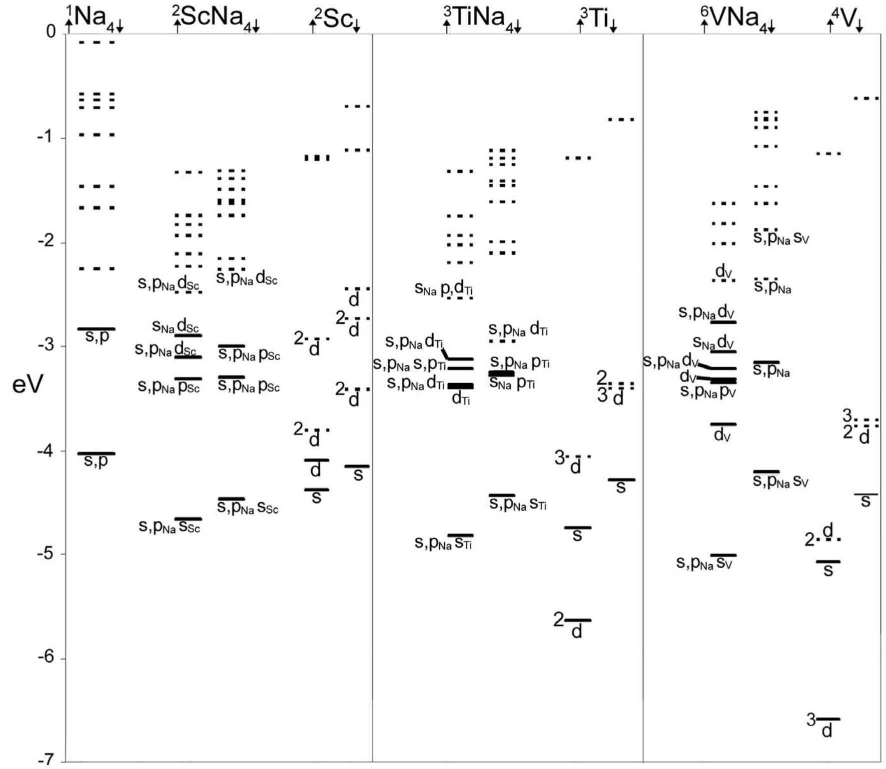

FIG. 2. One-electron levels (in eV) in Na_4, ScNa_4, Sc, TiNa_4, Ti, VNa_4, and V. Superscripts indicate the spin multiplicity. The continuous lines represent occupied levels; the dotted lines correspond to unfilled states. The degeneracy is marked by a number next to the level. The angular characters of the energy levels are also given. The arrows indicate the majority (up) and minority (down) spin states.

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 the quenching of atomic moments. Here, hybridization along with a large exchange splitting has an opposite effect. For example, exchange splittings (defined as the energy difference between the highest α-spin MO and the lowest β-spin MO having predominantly *d* characters) in TiNa_6 and VNa_6 clusters are ~1 and ~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.*[13] is of some impor-

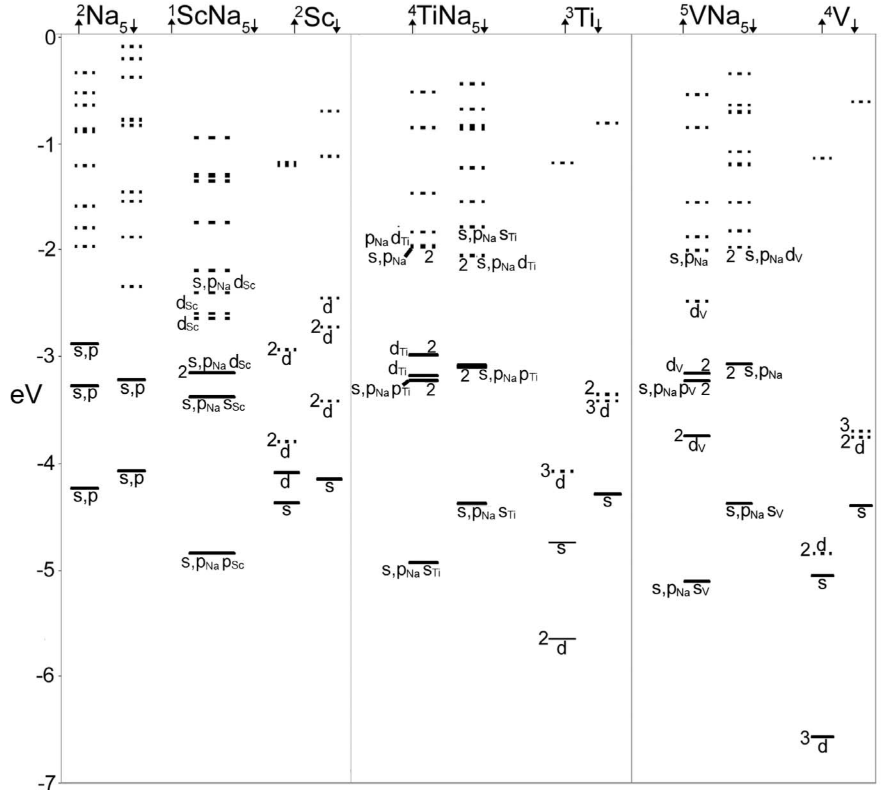

FIG. 3. One-electron levels (in eV) in Na_5, ScNa_5, Sc, TiNa_5, Ti, VNa_5, and V. Superscripts indicate the spin multiplicity. The continuous lines represent occupied levels; the dotted lines correspond to unfilled states. The degeneracy is marked by a number next to the level. The angular character of the energy levels is also given. The arrows indicate the majority (up) and minority (down) spin states.

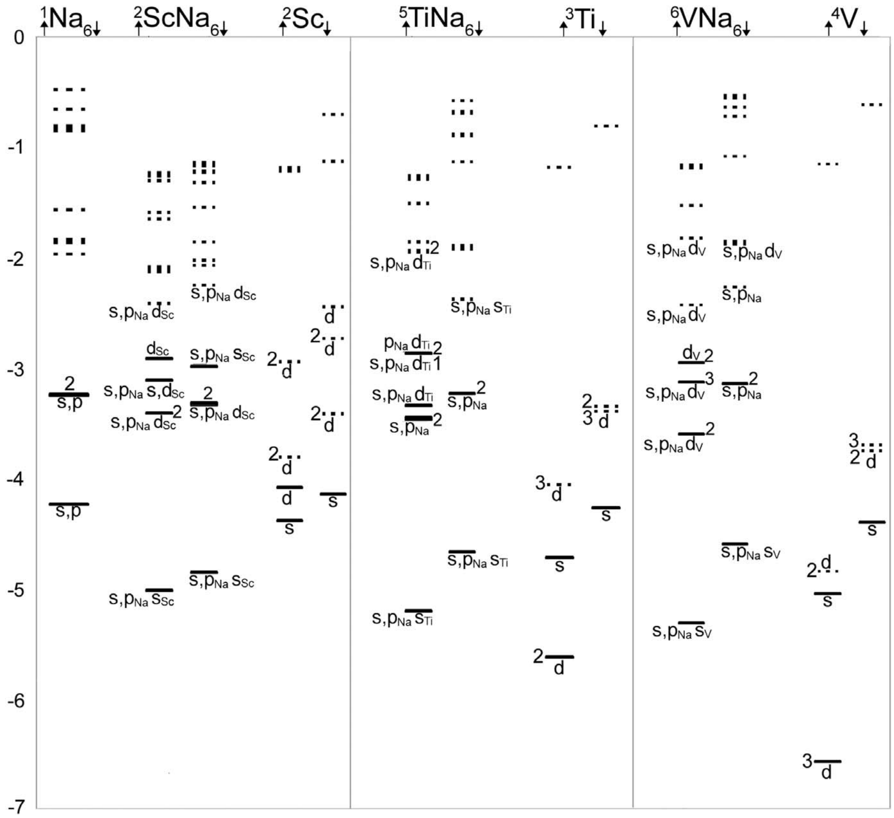

FIG. 4. One-electron levels (in eV) in Na_6, $ScNa_6$, Sc, $TiNa_6$, Ti, VNa_6, and V. Superscripts indicate the spin multiplicity. The continuous lines represent occupied levels; the dotted lines correspond to unfilled states. The degeneracy is marked by a number next to the level. The angular character of the energy levels is also given. The arrows indicate the majority (up) and minority (down) spin states.

tance here. In the Au_6 cluster, the TMs 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 MOs 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 MOs 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 an (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.*[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 $TMNa_n$ clusters can be measured by the embedding energy (EE) of the TM in the Na_n cluster. This is defined as

$$\mathrm{EE}(\mathrm{TMNa}_n) = E(\mathrm{Na}_n) + E(\mathrm{TM}) - E(\mathrm{TMNa}_n), \tag{2}$$

where $E(\mathrm{TMNa}_n)$ is the ground state total energy of a TM doped Na_n cluster, $E(\mathrm{Na}_n)$ is the total energy of a pure Na_n cluster, and $E(\mathrm{TM})$ 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.[35,36] 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-Witmer spin conservation rule.[36] 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 have been considered, whichever gives a larger EE. The calculated EEs 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_4 to Na_6, 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 6.6–7 μ_B as found in the experimental studies of Bergmann and Song.[15,16] Our preliminary calculations show that large moments survive on the

Ti and V doped Na_n clusters at least up to $n=9$.[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 I. All the clusters have a large gap of ~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. The present results for VNa_n clusters support the conclusions of the experimental studies by Bergman and Song[15,16] that the V atoms supported on alkali layers can attain large spin moments. ScNa_6 cluster also has a large moment of 3 μ_B in a low lying isoenergetic state. An analysis of the MOs 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.

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