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Enhanced magnetic moments of alkali metal coated Sc clusters: New magnetic superatoms

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It is shown that the magnetic moments of Sc atoms can be significantly enhanced by combining them with alkali atoms. We present results of first principles electronic structure calculations of ScNa_n ($1 \leq n \leq 12$) clusters that indicate that a ScNa_{12} cluster consisting of a Sc atom surrounded by 12 Na atoms forming a compact icosahedral structure has a spin magnetic moment of $3\mu_B$ that is three times that of an isolated Sc atom. This unusual behavior is analyzed in terms of the filling of the supershells 1S, 1P, ... controlled by the nature and size of the alkali atoms and the more localized Sc 3d orbitals that hybridize weakly with Na sp orbitals. It is shown that even larger magnetic moments could be attained by controlling the relative position of 1S, 1P, and 3d states. Indeed, our studies indicate large magnetic moment five times that of an isolated Sc atom in the ScK_{12} and ScCs_{12} clusters, in which the 3d orbitals of Sc adopt a half-filled configuration, while the clusters are stabilized by filled $1S^2$, $1P^6$, and $2S^2$ shells, the features making them as new magnetic superatoms. © 2010 American Institute of Physics. [doi:10.1063/1.3367722]

I. INTRODUCTION

One of the exciting developments in cluster science is the finding that the electronic states in small clusters of metal atoms can be reasonably described by a confined nearly free electron gas in a spherically symmetric potential.¹⁻⁵ The electronic states in such a system are grouped into shells 1S, 1P, 1D, 2S, ..., much in the same way as in atoms, although the differences in the radial form of potential leads to different combination of quantum numbers. This analogy has led to the idea that selected clusters could mimic the electronic behavior of atoms of similar valence states and hence be regarded as superatoms forming a third dimension to the periodic table.⁶⁻¹⁴ Over the past few years, Khanna and co-workers have proposed superatom mimics resembling halogen,^{6,8} alkaline earth,⁹ and multiple valence superatoms.¹⁰ Unlike atomic orbitals, the superorbitals 1S, 1P, 1D, ... are delocalized over the cluster. For nD ($n = 1, 2, \dots$) supershells, such a delocalization reduces the exchange coupling, and hence the stabilization of magnetic species through such supershells is less trivial. In a recent paper, the present authors proposed an alternate strategy to design magnetic species.¹⁴ We showed that the magnetic superatoms could be realized by having a composite cluster whose central site is a transition metal atom, while the surrounding atoms are the alkali atoms. The central atom with localized d-states can then stabilize a majority-spin manifold, while the surrounding atoms provide the energetic stability via supershells of S and P electrons. In particular we proposed VCs_8 and $\text{MnAu}_{24}(\text{SH})_{18}$ as magnetic superatom mimics with filled majority localized d-states breeding the

magnetism and delocalized supershell states providing stability. The magnetic coupling between molecules formed from such superatoms can be weak and tunable. In particular, we recently showed that molecules formed from such magnetic superatoms may lead to highly polarized currents.¹⁵

The combination of localized d-states and extended S, P, ... shells in such transition metal embedded simple metal motifs does offer other opportunities. For example, starting from the single transition metal atom, as the alkali atoms are successively added, the ordering of the supershells vis-à-vis the localized d-state could result in situations where the electrons fill the extended states or the localized d-states. This could lead to situations where the spin magnetic moment on the central atom could be enhanced much beyond its atomic limit by controlling the number and the nature of alkali atoms. Here we focus on ScNa_n clusters to demonstrate this intriguing effect. We investigate ScNa_n clusters containing up to 12 Na atoms needed to complete the first coordination shell around the central transition metal atom. The key issues we focus on are (i) if the Sc magnetic moment is enhanced, (ii) if the enhancement persists up to full coverage of the first coordination shell needed to have a geometrically compact motif, and (iii) if answers to (i) and (ii) are yes, then what could the electronic origin of such an enhancement be. Once we establish the underlying mechanism, we then demonstrate how an even larger magnetic moment could be realized using other alkali metals. Indeed, we show that a spin magnetic moment as high as five times that of an isolated Sc atom can be obtained in the ScK_{12} and ScCs_{12} that also have closed supershells and thus can be regarded as magnetic superatoms.¹⁴ We also examine the resilience of the resulting magnetic state by analyzing the energy separation between the ground state and the closest lying spin configuration.

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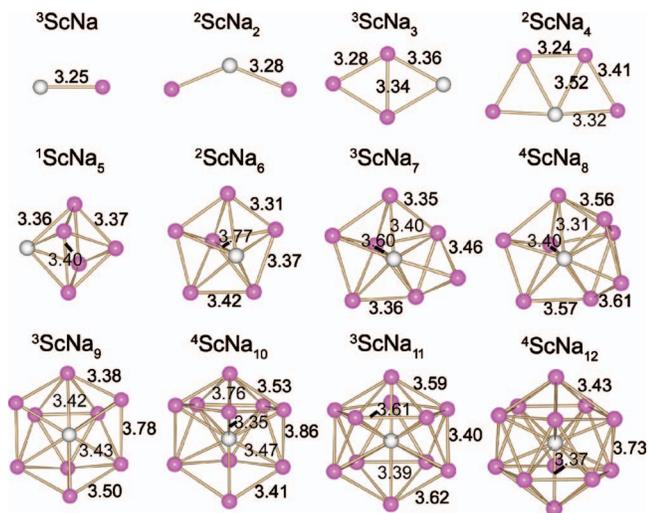


FIG. 1. Ground state geometries of the ScNa_n ($n=1-12$) clusters. The superscripts indicate spin multiplicity in the ground state. The bond lengths are given in angstrom.

Section II describes our theoretical approach, while Sec. III contains the results of our investigations and a discussion of results. Section IV is dedicated to final conclusions.

II. THEORETICAL METHODS

The theoretical studies were carried out within a linear combination of atomic orbitals molecular orbital approach implemented within the gradient corrected density functional theory framework.¹⁶ The calculations were performed using atom-centered Gaussian-type basis functions and the DEMON2K software.¹⁷ The PW86 (Ref. 18) gradient corrected exchange-correlation functional, all electron calculations for Na, K, and Sc based clusters with the double ζ valence plus polarization basis sets optimized for gradient corrected functionals,¹⁹ and the A2 auxiliary function set were used. The Cs atom was described using the nine electron quasiscalar relativistic effective core potential proposed by Leninger *et al.*²⁰ in combination with the corresponding basis set and the GEN-A2* auxiliary function set.

For each cluster size, the ground state search was carried out by starting from several initial geometries and possible spin states and optimizing the geometry. All structures were fully optimized without symmetry constraints employing the quasi-Newton method in delocalized redundant coordinates,²¹ and the stability of the resulting ground states was examined through a frequency analysis. The molecular geometries and orbitals were plotted using the SCHAKAL (Ref. 22) and MOLEKEL (Ref. 23) softwares, respectively. For more details about the numerical procedure, we refer the reader to previous publications.^{10,14} Using this approach we investigated ScNa_n clusters containing up to 12 Na atoms and the ScK_{12} and ScCs_{12} clusters.

III. RESULTS AND DISCUSSIONS

A. Sc doped sodium clusters

An isolated Sc atom has an electronic configuration of $3d^1$ and $4s^2$ and hence has one unpaired d electron. Figure 1

shows the progression of the geometry as successive Na atoms are added to a Sc. Small ScNa_n clusters containing up to four Na atoms have planar structures and ScNa_6 is the first cluster to have an interior Sc atom. As successive Na atoms are added, the structures evolve toward an icosahedral cage with a central Sc atom. We tried structures where the Sc atom was forced to occupy a surface site, while a Na atom was placed at the center. The resulting structures were all found to be higher in energy, indicating that the structures shown in Fig. 1 are the ground states. As mentioned previously, the optimization included both the geometry and the spin multiplicity. The spin multiplicities in the ground states are also marked in Fig. 1. For each cluster, the resiliency of each spin state was further examined by calculating allowed spin configurations above and below the ground state spin configuration. The relative energy (E_{rel}) between the ground state and the immediate higher energy isomer of different spin provides an idea about the spin stability of the ground state magnetic configuration.

In Table I, we show the atomization energy (AE), the gain in energy (ΔE) in forming the cluster from the preceding size, the spin magnetic moments of the ground state, and the spin magnetic moment of the immediate higher energy isomer as well as its relative energy E_{rel} . The AE represents the energy required to dissociate the cluster into individual atoms and was calculated using the expression

$$\text{AE} = E(\text{Sc}) + nE(\text{Na}) - E(\text{ScNa}_n).$$

Here $E(\text{Sc})$, $E(\text{Na})$, and $E(\text{ScNa}_n)$ are the total energies of a Sc atom, Na atom, and ScNa_n cluster. The AE presents a steady increase as a function of the number of Na atoms. We were particularly interested to identify more stable species, namely, the species that are energetically favorable. To this end, we examined the gain in energy in forming the larger cluster from the preceding size using the equation

$$\Delta E = E(\text{ScNa}_{n-1}) + E(\text{Sc}) - E(\text{ScNa}_n)$$

The results in Table I indicate that while the gain in energy range from 0.68 to 1.20 eV, slightly larger gain in energy of 1.20 and 1.17 eV occur in going from $\text{ScNa}_5 \rightarrow \text{ScNa}_6$, and $\text{ScNa}_{11} \rightarrow \text{ScNa}_{12}$, respectively. As we will show, the stability of ScNa_6 is related to a filling of the supershell electronic states. On the other hand, the stability of ScNa_{12} can be reconciled within a geometric shell closure known to occur in metallic clusters.

The main focus of the current work is the spin magnetic moment, and it is interesting to note that while the initial addition of Na atoms first quenches the spin magnetic moment at ScNa_5 , the moment reappears on further addition of Na atoms. To better visualize the trend, we plot the spin magnetic moment as a function of size in Fig. 2. The horizontal line corresponds to an isolated Sc atom. Out of all the clusters, only ScNa_5 has a zero net spin magnetic moment. For larger sizes, the magnetic moment shows an even-odd oscillation with clusters having an even number of Na atoms exhibiting a spin magnetic moment of $3\mu_B$, a moment three times that of an isolated Sc atom.

To understand these variations in moments, we carried out an analysis of the resulting cluster electronic orbitals. For

TABLE I. AEs, energy gain (ΔE), and magnetic moments (μ) of the ScNa_n clusters ($n=1-12$), K_{12}Sc , and Cs_{12}Sc . Magnetic moment of the immediate higher energy spin state and the energy difference with respect to the ground state (E_{rel}) are also given. All energies are in eV.

Cluster	Ground state			Lower energy	
	AE	ΔE	μ	$\mu(\mu_B)$	E_{rel}
NaSc	0.62		2	0	0.290
Na ₂ Sc	1.30	0.68	1	4	0.038
Na ₃ Sc	2.14	0.84	2	0	0.236
Na ₄ Sc	3.07	0.93	1	3	0.085
Na ₅ Sc	4.03	0.97	0	2	0.003
Na ₆ Sc	5.23	1.2	1	3	0.298
Na ₇ Sc	6.07	0.84	2	0	0.145
Na ₈ Sc	6.94	0.87	3	1	0.010
Na ₉ Sc	7.86	0.92	2	0	0.027
Na ₁₀ Sc	8.86	1.01	3	1	0.004
Na ₁₁ Sc	9.97	1.1	2	4	0.012
Na ₁₂ Sc	11.14	1.17	3	1	0.076
K ₁₂ Sc	8.15		5	3	0.102
Cs ₁₂ Sc	6.15		5	3	0.021

orbitals delocalized over the cluster, we examined the symmetry of the orbital to assign them superatom orbital designations. The other kind of electronic orbitals are those with appreciable Sc d-component. As the early 3d TM atoms have relatively large d orbitals and the sp orbitals in the alkali atoms are also fairly diffuse, there is a finite overlap of the 3d orbitals of Sc and the 3s and 3p orbitals of the Na atoms. For these hybridized electronic states, a Mulliken population analysis shows that they have around 70% of d-character, and consequently they are marked as 3d in Fig. 2. Note that such hybridization can lead to an effective change of d occupancy on the Sc atom.

Figure 2 shows that ScNa has a magnetic moment of $2\mu_B$ that corresponds to a $1S^2$, $1P^1$, and $3d^1$ configuration in which the three delocalized s-valence electrons (two from Sc and one from Na) adopt the $1S^2$ and $1P^1$ supershell configuration. The addition of a second Na atom to form ScNa₂ contributes one more s electron that occupies the $1P_\beta$ orbital and pairs with the $1P_\alpha$ electron, reducing the magnetic moment to $1\mu_B$ (α and β refer to majority and minority spin electrons). Successive addition of Na atoms continues filling the 1P shell until ScNa₅ in which the Sc and Na s-valence

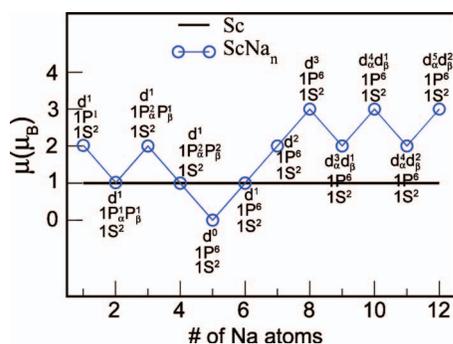


FIG. 2. Variation in the magnetic moments (μ) with n in the ScNa_n clusters with $n=1-12$. The magnetic moment of the Sc atom is also given as reference. The occupancy of delocalized 1S and 1P shells, and localized 3d atomic orbitals for each system is also given.

electrons and the d^1 Sc electron completed the $1S^2$ and $1P^6$ supershell and the moment is quenched. This is clearly seen in supporting Fig. S1,²⁴ where we show the electronic levels and the associated orbital charge density isosurfaces. Starting from ScNa₅, further addition of Na atoms begins to fill the 3d Sc atomic orbital enhancing the magnetic moment. Unfortunately, the reduced exchange energy in the ScNa_n species favored the occupancy of the $3d_\beta$ levels, and the largest moment that can be attained is $3\mu_B$ (Fig. 2). In this way, the ScNa₁₂ cluster has a net d^7 configuration and presents an enhanced magnetic moment of $3\mu_B$ as illustrated by the one-electron energy levels in Fig. 3. The cluster is marked by a

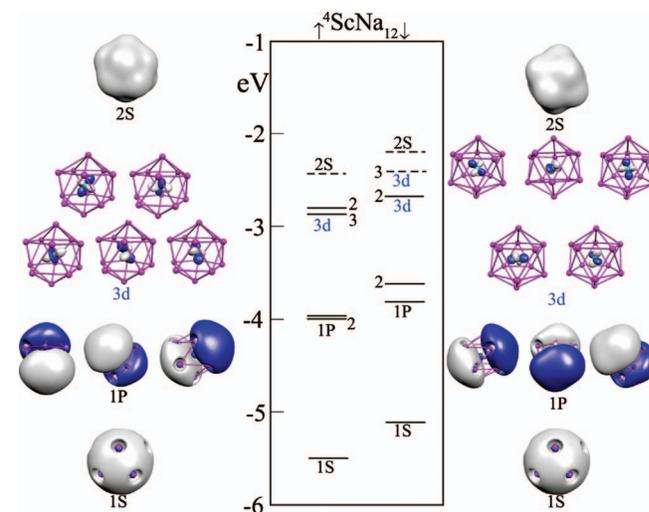


FIG. 3. One-electron energy levels (in eV) and molecular orbital charge density isosurfaces (isoval=0.05 a.u. for 3d and 0.005 a.u. for 1S, 1P, and 2S orbitals) in ScNa_{12} . Superscript indicates the spin multiplicity. The continuous lines represent occupied levels; the dotted lines correspond to unoccupied states. The degeneracy is marked by a number next to each level. The angular characters of the levels with upper-case letters for delocalized 1S and 1P shells, and lower-case letters for localized 3d atomic orbitals are also given. The arrows indicate the majority (up) and minority (down) spin states.

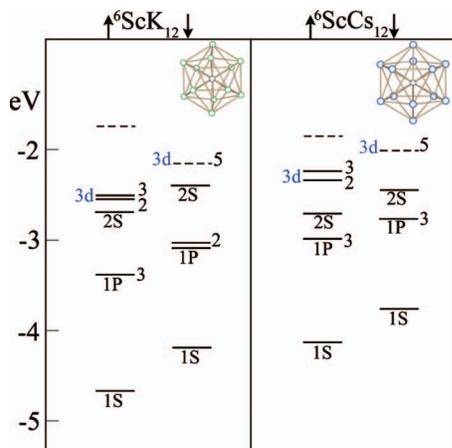


FIG. 4. One-electron levels (in eV) in ScK_{12} and ScCs_{12} . The optimized geometries are also given. Superscripts indicate the spin multiplicity. See caption of Fig. 3.

closed geometric shell leading to a larger gain in energy as it is formed from ScNa_{11} . Note also that as shown in Fig. 3, the lowest unoccupied states are the diffuse 2S levels. If they could be moved down, one could enhance the moment.

Before we proceed toward controlling moment, we investigated the resiliency of the spin state through studies of the E_{rel} . Table I shows our calculated E_{rel} as a function of size. Note that ScNa_n clusters containing 8–11 Na atoms have magnetic isomers, i.e., states with differing multiplicity close to the ground state. For ScNa_{12} , on the other hand, the closest magnetic state is 0.08 eV higher in energy indicating that the ground state in this cluster is relatively more robust.

We would like to add that while Na_2Sc , Na_4Sc , Na_5Sc , Na_6Sc , and Na_{11}Sc have states with higher spin moment close to the ground state; the remaining clusters have lowest excited states with lower spin moments. This could lead to interesting variations in the observed moments in experiments at different cluster temperatures.²⁵

B. Sc doped $\text{K}_{12}/\text{Cs}_{12}$ clusters

One way to enhance the magnetic moment of the mixed clusters could be to stabilize the 2S shell so that it gets filled before the minority 3d states. This could be accomplished by reducing the sp-d hybridization as well as moving the 2S state. The reduced hybridization will maintain larger atomic exchange splitting between majority and minority d-states, while the 2S stabilization would occupy the extra two electrons. A possible way to accomplish this may be to try a bigger alkali atom. The larger size of the alkali will reduce the s-d mixing and may stabilize the 2S state. Could K and Cs do the needful?

To test our idea, we studied structures for ScK_{12} and ScCs_{12} , and we also got in these two cases the same icosahedral geometry such as that of ScNa_{12} as the ground state. However, interestingly, we do get a magnetic moment of $5\mu_B$ in these clusters. To probe the origin of such a large spin magnetic moment, we examined the one-electron levels in ScK_{12} and ScCs_{12} clusters. These are shown in Fig. 4. Unlike the case of ScNa_{12} , all the five d type molecular orbitals (MOs) of the majority spin (α) and none of the d type MO's

of the minority spin (β) get occupied in the Sc atom surrounded by K/Cs atoms. This gives the optimum d^5 configuration, which leads to large magnetic moment of $5\mu_B$, while the nearly free electron gas adopts the $1S^2$, $1P^6$, and $2S^2$ configuration. As we recently proposed, such clusters stabilized by filled supershells along with half-filled d-level (filled majority levels) can be regarded as magnetic superatoms. To further prove the stability of ScK_{12} and ScCs_{12} magnetic superatoms, we also calculated the AE and E_{rel} as reported in Table I.

Thus our guess of large magnetic moments in ScK_{12} and ScCs_{12} clusters because of optimized sp-d hybridization and 2S stabilization turned out to be true. If we analyze the structure of ScNa_{12} , ScK_{12} , and ScCs_{12} , which are all icosahedral, the distance between Sc and Na atoms is 3.37 Å, between Sc and K atoms is 4.15 Å, and between Sc and Cs atoms is 4.86 Å. Based on these distances we can calculate the available spherical volume inside the Na_{12} , K_{12} , and Cs_{12} cages. The radii for these are found to be 1.51, 1.95, and 2.26 Å, respectively. So when we go from a Na to a K and Cs host, an increase in the volume inside the cage for Sc atom leads to the correct mixing of sp-d orbitals for optimum d^5 configuration, and we get large magnetic moments. However, we would like to emphasize a few important points as we go from a K_{12} to a Cs_{12} host. Even though the next higher energy spin isomers of both clusters are of spin magnetic moment $3\mu_B$,

- (i) the relative energy (E_{rel}), as shown in Table I, indicates that the spin magnetic moment of $5\mu_B$ is much more stable in ScK_{12} compared to ScCs_{12} ; so when we increase the size of the alkali metal taking Cs instead of K, the sp-d hybridization strength decreases due to the E_{rel} value that decreases quite considerably; and
- (ii) the geometry of the next isomer in ScK_{12} is icosahedral, such as the ground state geometry.

In the case of ScCs_{12} , the next isomer has distorted icosahedral geometry with one Cs atom being at a larger distance. There being only 11 neighboring Cs atoms, the sp-d hybridization changed, leading to a d^3 configuration and a spin magnetic moment of $3\mu_B$.

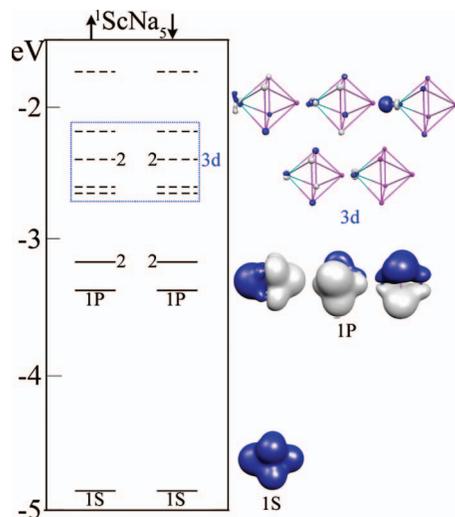
IV. CONCLUSIONS

We have shown that the addition of alkali atoms to a Sc atom can result in large spin moments. The enhancement is controlled by the relative ordering of the supershells, more localized 3d states, and the exchange splitting of the d-states. We demonstrate how these can be controlled by changing the alkali atom that modulates the position of the supershell states as well as the hybridization between the 3d and the sp-states located on the alkali atoms. The studies predict a spin magnetic moment five times that of an isolated Sc atom in the ScK_{12} and ScCs_{12} magnetic superatom clusters, in which the 3d orbitals of Sc adopt a half-filled configuration, while the systems are stabilized by a $1S^2$, $1P^6$, and $2S^2$ supershells.

We are now extending these investigations to explore if similar effects occur in other mixed clusters. We hope that the present findings would stimulate experimental work to probe the spin states.

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