Growth model investigation of Vanadium-Benzene Polymer

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Abstract

Electronic and magnetic properties of $V_nBz_{n+1}$ sandwich clusters are investigated using density functional theory. Growth model is applied to investigate the property change of Vanadium-Benzene sandwich clusters. Our results show that, for $n\leq8$, all V ions tend to put their spin in ferromagnetic state, and that the magnetic moments of $V_nBz_{n+1}$ increase linearly with $n$. Finite-size effects induce a nonmonotonous behavior of the $V_nBz_{n+1}$ magnetic properties. In the case of $n=8$, the electronic properties of $V_nBz_{n+1}$ has the same characteristics with the counterpart of Vanadium-Benzene infinite wire, hence, the critical length of $V_nBz_{n+1}$ is defined eight. Furthermore, our results demonstrate that Vanadium-Benzene infinite wire is a proper material for spin polarized transport and has a high stability in the presence of external electronic and magnetic fields.

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I. INTRODUCTION

Recently, one kind of one-dimensional transition-metal based molecular magnets have attracted great attentions,[1–9] because these molecular magnets are considered as potential material used in recording media and spintronics devices. Among all of them, $V_n Bz_{n+1}$ sandwich clusters are a hot object and have a linear structures and ferromagnetic ground states, those clusters were suggested to be a proper material for spintronics devices, especially for spin filter and spin-polarized transportation. Experimental studies suggested that, for $n \leq 4$, $V_n Bz_{n+1}$ sandwich clusters have a one-dimensional structure and possess the magnetic moments increasing monotonously with $n$. Theoretical investigations on $V_n Bz_{n+1}$ provided farther information for those structural and magnetic properties. Maslyuk et al. [10] found that $V_3 Bz_4$ placed between magnetic Ni or Co electrodes will act as almost perfect spin filter, and that the spin polarization of the current can reach 90%. Koleini et al. [11] also used spin density functional theory and nonequilibrium Green’s function to investigate the transport properties of $V_n Bz_{n+1}$ placed between graphene or single-wall carbon-nanotube, their results showed that spin polarization of the current could reach as high as 99%, and that the polarization increased with cluster size increased. In the case of Vanadium-Benzene infinite wire ($V(Bz)_{\infty}$), a spin polarized density of states around Fermi Surface was found by Xiang et al. [12], thus $V(Bz)_{\infty}$ was deemed to a perfect material for spin-polarized current transport.

As mentioned above, $V_n Bz_{n+1}$ and $V(Bz)_{\infty}$ may be an ideal material for recording and spin-polarized transport. However, it is very important to find out the link between $V_n Bz_{n+1}$ and $V(Bz)_{\infty}$, in other words, critical length in which the magnetic clusters have the same properties as $V(Bz)_{\infty}$ is a key parameter for practical applications and theoretical studies. Additionally, since $V_n Bz_{n+1}$ and $V(Bz)_{\infty}$ are expected to be used in recording and spin-polarized transport, they will inevitably endure the interference of external electronic and magnetic fields, and the stability of $V(Bz)_{\infty}$ in the presence of external electronic and magnetic fields is also an interesting issue. Hence, in this work, we will mainly discuss the critical length of $V_n Bz_{n+1}$ using growth model and the stability of $V(Bz)_{\infty}$ in the presence of external electronic and magnetic fields.

This paper is organized as follows: the computational method and theoretical model are briefly described in Sec. II; the results and discussions are presented in Sec. III; and a brief
II. COMPUTATIONAL DETAILS

The linear sandwich of $V_nBz_{n+1}$ is constructed as the following. Firstly, the most stable structure of $VBz_2$ is obtained by performing the full relaxation. For the ground state of $V_2Bz_3$, $VBz$ is added to the stable $VBz_2$ with the added Bz rotating $0^\circ$, $15^\circ$, and $30^\circ$, respectively, furthermore, the magnetic moment of the added V is placed in the direction of up and down. Therefore, on the base of the optimized $VBz_2$, six different initial structures, which are fully relaxed without any symmetry constraint, are used for searching the ground state of $V_2Bz_3$. Following the same way, the completely relaxed ground states of $V_nBz_{n+1}$ are obtained from the optimized $V_{n-1}Bz_n$. This process is named as the growth model which is widely used in cluster science. As far as we know, it is the first time that growth model is applied on this kind of molecular magnets. In our opinion, the growth model can simulate the growth process of $V_nBz_{n+1}$ more accurately.

The properties of $V_nBz_{n+1}$ and $V(Bz)_\infty$ are calculated based on the density functional theory,[16] and the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof functional[17] is used. Valence electrons are expanded by linear combination of numerical atomic orbital formalism as implemented in SIESTA code[13–15], and core electrons are described by the Troullier-Martins pseudopotentials.[18] We use double-$\zeta$ basis (DZ) for C and H orbitals and a double-$\zeta$ basis plus polarization (DZP) for the transition metal orbitals. We have fully tested them on the properties of benzene, methane and bulk V, in which the results agree well with experimental values or full-electron calculations.

All the atomic positions are fully relaxed until forces are less than 0.04 eV/Å and the convergence criterion for density matrix is $10^{-4}$.

III. RESULTS AND DISCUSSIONS

The optimized sandwich $VBz_2$ with $D_{6h}$ symmetry has an integer magnetic moment of $1\mu_B$. V has a localized magnetic moment (1.23$\mu_B$), and benzene are anti-parallelly polarized with the magnetic moment of $0.115\mu_B$ distributed over 6 C atoms. Also, $V_2Bz_3$ has the $D_{6h}$ symmetry, and the rotated states with the edge Bz rotating $15^\circ$ and $30^\circ$ are semi-stable...
configurations. These structural characteristics are maintained until \( n \) increases to 8. As shown in Table I, the total energies of \( V_n B_{n+1} \) increase with the rotation angle of the edge Bz increasing. This phenomenon also appears in \( V(Bz)_\infty \).[10]

It is one of our purposes to find the link between \( V_n B_{n+1} \) and \( V(Bz)_\infty \) for practical applications and theoretical studies. We will use the growth model described above to search the critical length of \( V_n B_{n+1} \) by inspecting the electronic properties of \( V_n B_{n+1} \) and \( V(Bz)_\infty \). Fig. 1 presents the evolution of the density of states (DOS) of \( V_n B_{n+1} \) from \( n = 1 \) to \( n = \infty \). When the number of \( n \) closes to 8, the DOS of \( V_n B_{n+1} \) has similar characteristics with the counterpart of \( V(Bz)_\infty \), especially around Fermi Level. Hence, eight layer is the critical length for \( V_n B_{n+1} \). After \( n \geq 8 \), the properties of \( V_n B_{n+1} \) do not change remarkably. Note that, in the cases of \( V_n B_{n+1} \), there are additional states distributed from -5 eV to -4 eV compared with the DOS of \( V(Bz)_\infty \). These isolated states are from the edge benzenes. Because there are two edge benzenes for any one of \( V_n B_{n+1} \), the magnitude and shape of the isolated states do not change as \( n \) changes from 1 to 8. In order to further confirm the critical length is 8, the properties of \( V_9 B_{10} \) are investigated, the DOS of \( V_9 B_{10} \) is shown in the inset (a) of Fig 2, we can found that, around the Fermi Level, the DOS of \( V_9 B_{10} \) changes very weakly comparing with the counterpart of \( V_8 B_9 \) and has similar characteristics with the DOS of \( V(Bz)_\infty \). The DOS of \( V(Bz)_\infty \) around Fermi Surface shown in Fig. 1(h) is polarized and thus \( V(Bz)_\infty \) is expected to be a proper material for spin-polarized transport.

The total energy calculations exhibit that all \( V_n B_{n+1} \) have ferromagnetic ground states, in other words, the added V ion intends to put his magnetic moment parallel with other V ions. As seen in Fig. (2), the magnetic moments of \( V_n B_{n+1} \) increase linearly with the number of V ions increasing, which is consistent with the experimental results (\( n \leq 3 \))[6] and theoretical investigation for \( n \leq 6 \).[7] However, the added V ion has an anti-parallel magnetic moment with the other V ions named as anti-ferromagnetic states is a second stable state. The energy difference, which can be deemed to the energy costing(ES) to inverse the magnetic moment of edge V ion, between the second stable and ground state are shown in Table II. An nonmonotonous behavior of ES is shown in Table II, from \( n = 2 \) to \( n = 4 \), ES increases with \( n \) in accord with Weng’s results.[19] Whereas, ES decreases from 102 meV to 67 meV while \( n \) changing from 4 to 5. For \( n \leq 8 \), the drastic variations of ES due to finite-size effects are found. In order to confirm this phenomenon, we do not take into account the structural relaxation, but only the magnetic interaction between the edge
V ion and the other V ions are considered. Hence, all atomic positions are fixed and V-Benzene distance is fixed as 1.70Å. The data appearing in the no-relaxation row of Table II also clearly present the nonmonotonous behavior. The same phenomenon were found in magnetic anisotropy of one-dimensional nanostructures of transition metals\[20, 21\], where Dàvila et al.\[20\] reported strong oscillations of the magnetic anisotropy energy as the length of the one-dimensional chains.

As mentioned above, \(V_{\text{Bz}}^{n+1}\) and \(V_{\text{Bz}}^\infty\) are seem to be an deal materials for recording and spin-polarized transport. While \(V_{\text{Bz}}^{n+1}\) and \(V_{\text{Bz}}^\infty\) are used for spintronics devices, they will be exposed to additional electronic and magnetic fields. External fields can influence the properties of magnetic materials strongly, for example, Son et al.\[22\] found that the magnetic properties of graphene nanoribbons can be controlled by the in-plane external electric fields applied through the zigzag-shaped edges. Also, in some magnetic systems, heat, pressure and magnetic field\[23\] can induce the spin-crossover phenomenon which originates from the transition between the different spin states. Spin-crossover complexes include organo-metals\[24\] and diluted magnetic semiconductors.\[25\] The main characteristics of spin-crossover complexes is multi-spin states, hence, the total energies of \(V_{\text{Bz}}^\infty\) unit cell are calculated with the magnetic moment fixed. The calculated total energies vs total magnetic moment shown in Fig. (3) implicit that there are only one minimum located at 1\(\mu_B\) for \(V_{\text{Bz}}^\infty\), which means that multi-spin states do not exist in \(V_{\text{Bz}}^\infty\). Therefore \(V_{\text{Bz}}^\infty\) will be a stable material in the presence of magnetic field. Furthermore, we apply a transverse electronic field paralleled to benzene molecule \(V_{\text{Bz}}^\infty\), and tune the magnitude of electronic field from 0.0 eV/Ang to 0.5 eV/Ang. The DOSs of \(V_{\text{Bz}}^\infty\) in the presence of 0.0 ev/Ang and 0.5 ev/Ang electronic field are shown in Fig. (4). The electronic structure and magnetic moment of \(V_{\text{Bz}}^\infty\) almost are not changed in the presence of external electronic field. In a word, \(V_{\text{Bz}}^\infty\) has good stability in the presence of electronic and magnetic field.

IV. SUMMARY

We have systematically investigated the structural, electronic and magnetic properties of \(V_{\text{nBz}}^{n+1}\) \((n\leq8)\). In the case of \(n=8\), the electronic structure of \(V_{\text{nBz}}^{n+1}\) has the same characteristics with the counterpart of \(V_{\text{Bz}}^\infty\), hence, eighth-layer is the critical layer of
$V_n Bz_{n+1}$. In these $V_n Bz_{n+1}$ system, V ions are arranged in ferromagnetic state. Meaningfully, our results reveal an interesting nonmonotonous magnetic behavior caused by finite-size effect, and the energy cost for reversing the magnetic moment of the edge V oscillates with $n$. $V(Bz)_\infty$ is a proper material for spin-polarized transport and has high stability in the presence of electronic and magnetic field.

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TABLE I: The calculated total energy (relative to the lowest energy configuration of 0° rotation) of $V_n B_{z_{n+1}}$ with the new added benzene rotating 15° and 30°.

| meV | $V_2 B_z$ | $V_3 B_z$ | $V_4 B_z$ | $V_5 B_z$ | $V_6 B_z$ | $V_7 B_z$ | $V_8 B_z$ |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 15° | 10        | 20        | 81        | 35        | 61        | 12        | 12        |
| 30° | 25        | 44        | 95        | 69        | 92        | 25        | 36        |
TABLE II: The energy costing (ES) to inverse the magnetic moment of edge V ion in the cases of growth-model and no-relaxation, respectively.

|        | meV | V₂Bz₃ | V₃Bz₄ | V₄Bz₅ | V₅Bz₆ | V₆Bz₇ | V₇Bz₈ | V₈Bz₉ |
|--------|-----|-------|-------|-------|-------|-------|-------|-------|
| growth-model | 1   | 8     | 102   | 67    | 73    | 60    | 47    |
| no-relaxation | 10  | 3     | 90    | 120   | 84    | 69    | 51    |
FIG. 1: The total DOS of $V_nB_{n+1}$ ($n \leq 8$) and $V(Bz)_\infty$. The vertical dashed line represents the Fermi level.

FIG. 2: Total magnetic moments of $V_nB_{n+1}$ as a function of $n$, and the DOS of $V_9B_{10}$ and views of $V_7B_8$ are shown in (a) and (b) of the inset, respectively.

FIG. 3: The total energy vs the magnetic moment of $V(Bz)_\infty$.

FIG. 4: The total DOS of $V_nB_{n+1}$ in the presence of external electronic field, (a) and (b) for the electronic field are 0.0 eV/Ang and 0.5 eV/Ang, respectively.
Fig. 1 Wang.eps
Fig. 2  Wang.ep
Fig. 3 Wang.ep
Fig. 4  Wang.eps