PHYSICAL REVIEW B **78**, 020409(R) (2008)

Magnetism enhanced layer-like structure of small cobalt clusters

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(Received 13 October 2007; revised manuscript received 5 July 2008; published 29 July 2008)

The atomic and electronic structures of Co_N clusters ($13 \leq N \leq 23$) are studied by density-functional calculations with generalized gradient approximation. Surprisingly, it is found that Co_N clusters appear in layer-like (rather than icosahedral) structures with hcp or fcc stacking, which can be considered as a small fragment of bulk structure. Two structural transitions are identified, in coincidence with photoelectron spectroscopy measurement. The stability of layer-like structures is proved to be enhanced by magnetization.

DOI: 10.1103/PhysRevB.78.020409 PACS number(s): 75.75.+a, 36.40.Cg, 36.40.Mr, 73.22.−f

Nanomagnetism is a cutting-edge research field and may potentially revolutionize storage, sensing, spintronics, and optoelectronic technologies. One of the major focuses in this context is to search the ground-state structures of nanoclusters as the cluster size is reduced to a few tens of atoms. It is generally accepted that the cluster structure sensitively depends on the size and interatomic bonding behavior.[1–4] For instance, carbon, a strong covalent element, adopts fullerene structure in the cluster;[5] gold, a noble metal with closest packing structure in its bulk phase, shows planar structures for small clusters and cage structures at the medium size.[6–9] Aluminum clusters and some transition-metal clusters usually have icosahedral structures.[10–17] Obviously all these structures are different from their bulk counterparts.

3*d* transition-metal clusters have received particular attention,[15–20] due to potential applications in high-density storage and catalysis. Earlier studies demonstrated that Co_{13} and Ni_{13} have the icosahedral structure. It was proposed in later studies that Co_N and Ni_N clusters also adopt icosahedral-like structures up to $N=55$.[21–23] Nevertheless, this is considered well established only for Ni clusters,[23–25] whereas for Co it is still a conjecture based on the similarity between Co and Ni. Indeed, this was challenged by recent theoretical and experimental studies.[26–29] For example, photoelectron spectrum (PES) measurement[26] reveals major differences between Ni_N and Co_N clusters for $N=2-32$. The PES features of Co clusters show clearly two transitions from $N=15$ to $N=16$ and from $N=19$ to $N=20$. No such transition is observed for Ni clusters in the same range. Although icosahedron was assigned as the ground-state structure of Co_{13},[27] a biplanar structure was recently found to be more stable. This triggers a great deal of interest in exploring noncompact structures of transition-metal clusters.[28,30–32] Obviously, systematic studies of structural features and growth modes of Co clusters are necessary to clarify various issues in the field.

In this Rapid Communication we report extensive first-principles study of atomic and electronic structures of Co_N ($N=13-23$) clusters. Surprisingly it is found that small Co clusters show layer-like structures, encompassing two or three (111) planes of fcc lattice. Therefore Co clusters can be considered as a fragment of bulk Co, in a way that is entirely different from Ni.

Present calculations are based on density-functional theory with generalized gradient approximation [33] implemented in the VASP code.[34] We use a cubic supercell of side length of 20.0–24.5 Å, together with periodic boundary condition. Only the Γ point is used to represent Brillion zone. The interaction between valence electrons and ion cores is described by the projector augmented wave potential,[35] while the wave functions are expanded in plane waves with a cutoff energy of 268 eV. The smearing parameter for total energy and density-of-states (DOS) calculation is 0.2. In order to examine the convergence of the present parameters, we calculated the bond length of a Co dimer and the nearest-neighbor distance in the bulk Co. The results are 1.962 and 2.500 Å, respectively, in close agreement with data of other computational (1.970 Å for dimer and 2.510 Å for bulk) and experimental (2.510 Å for bulk) works.[36]

As the initial guess of the structures for each size, we constructed several structural configurations with different symmetries and also took into account several amorphous motives acquired as metastable structures from simulated annealing which is implemented by empirical potential.[37] Structures of other species in recent references are also included.[12,22,30,31,38] The icosahedral-like structures, which grow according to the 13-atom icosahedron pattern, were proposed as the ground states for Co_N clusters up to $N=55$.[21,39] The typical icosahedral-like structures of Co_{19} and Co_{23} can be seen as two or three 13-atom icosahedral building blocks penetrating into each other. For purpose of a systematic comparison, we also include this type in our calculation. Due to the magnetic nature of cobalt, all calculations are carried out with spin-polarization functional.

Figure 1 shows all the ground-state structures of Co_N ($N=13-23$) clusters. Clearly, all of them can be viewed as layer-like structures. The binding energies of all the layer-like ground-state structures are shown in Fig. 2(a), while the energy gains over the icosahedral-like structures are shown in Fig. 2(b). The energy difference is typically as large as 0.6 eV, while the largest value reaches about 1.60 eV for Co_{13} and Co_{19}.

Particularly, the structure of Co_{13} is biplanar with seven or six atoms in each layer. The binding energy of this structure is about 1.63 eV higher than that of its icosahedral counterpart. Even compared with the buckled biplanar (BBP) structure recently proposed for Co_{13},[27] our structure is more stable in energy by 0.72 eV. The main difference between the present bilayer structure and BBP structure lies in the layer of six atoms. The BBP structure has a square of four atoms capped with two atoms at the opposite edges, while in the present bilayer structure six atoms are coplanar and form an

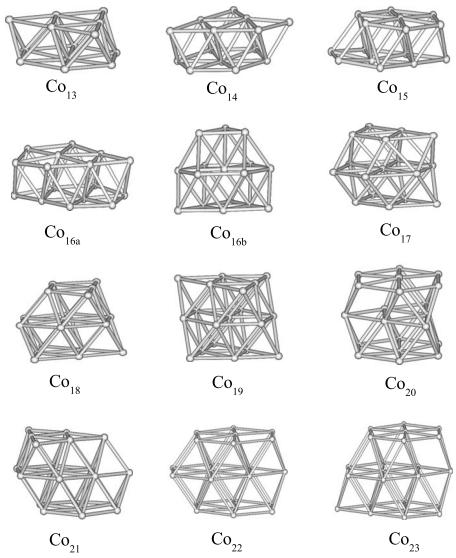

FIG. 1. The ground-state structure of $Co_{13}-Co_{23}$ clusters. Both bilayer structure of Co_{16a}, which is the ground state of neutral Co_{16}, and trilayer structure of Co_{16b}, the ground state of Co_{16}^-, are presented.

equilateral triangle. The symmetry of the bilayer structure (C_{3v}) is higher than that of BBP structure (C_{2v}). It should be noted here that this structure has also been discussed by Wang and Johnson[32] as a model motif for Co and other transition-metal clusters,[4] while its robust stability is confirmed by present work.

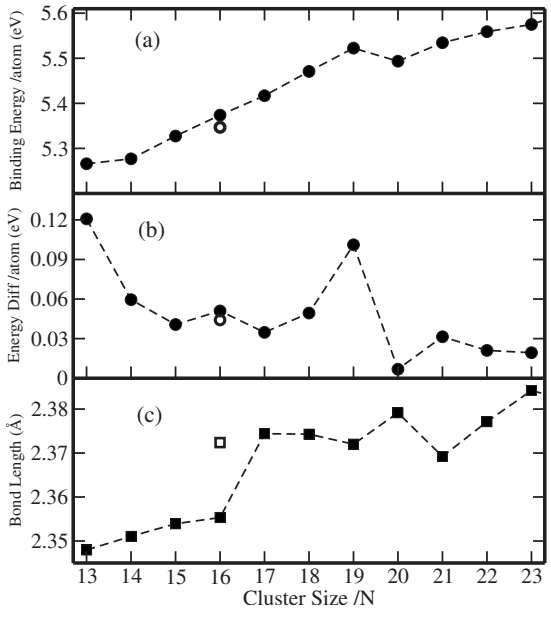

FIG. 2. (a) Binding energy of Co_N cluster with layer-like structure. Open circle marks the value for Co_{16b} structure. (b) Difference of binding energy between layer-like structures and their icosahedral-like counterparts. Open circle also for Co_{16b} structure. (c) Average bond length of layer-like structures (solid squares). Open square at $N=16$ is for Co_{16b}. The abrupt rise at $N=16$ corresponds to structural transition. Note that the value of Co_{16b} is quite higher than that of Co_{16a} but close to those of the larger three-layer structures.

When N increases, the bilayer structures continue to be energetically favorable until $N=16$. The structures of Co_{14}, Co_{15}, and Co_{16} (Co_{16a} in Fig. 1) can be obtained by capping one, two, and three atoms on a side surface of Co_{13}. Therefore Co_{13} can be considered as a seed of Co_{14}, Co_{15}, and Co_{16}. During our extensive search, we found that Co cluster tends to not have a layer with more than eight atoms, as clearly demonstrated in Fig. 1. This indicates that the bilayer structure cannot be favorable for $N>16$. For Co_{16}, we found that the second most stable isomer is a trilayer structure (Co_{16b} in Fig. 1), with the binding energy 0.11 eV lower than that for Co_{16a}. The difference between the bilayer and trilayer structures lies in the positions of three atoms added on Co_{13}. In the bilayer structure, these three atoms take one of the three side surfaces of the Co_{13}, while in the trilayer structure they stack on the seven-atom layer. Trilayer structures are also included in searching of smaller sizes ($N<16$), and they are found to be unstable with the binding energy typically 0.7 eV lower than those of their bilayer counterparts.

We found that the charging on Co_{16} drives the trilayer structure to be more stable than the bilayer structure. In anionic state, the trilayer structure is more stable than the bilayer one by 0.04 eV in energy. Although this is a tiny difference, the reversed relative stability shows that $N=16$ is the critical point for the transition between the bilayer and trilayer structures for Co clusters.

From $N=17-23$, all clusters have the trilayer structure as shown in Fig. 1. One still can see the bilayer Co_{13} kernel in the Co_{18}, Co_{19}, and Co_{20} clusters. It is interesting to point out another major change in atom arrangement from Co_{19} to Co_{20}. The structure of Co_{19} is a perfect regular octahedron of O_h symmetry, with three atoms in each edge, as shown in Fig. 1. Co_{18} has one atom less than Co_{19}, and both of them can be considered as a fragment of the fcc lattice. However, Co_{20} and larger clusters cannot be assigned as a fragment of the fcc lattice, but rather they are more like fragments of the hcp lattice with the *ABAB* stacking. Such transition of cluster structure, along with the bilayer to trilayer transition around $N=16$, directly causes the alternation of corresponding electronic features as will be discussed below. $Co_{21}-Co_{23}$ also adopt hcp-like stacking, but Co_{21} is not from Co_{20} with one more atom capped. In fact, all these three structures can be obtained by packing a triangle or hexagonal plane consisting of six or seven atoms onto the former two-layer structure Co_{15} or Co_{16}.

The transition from the bilayer structure to the trilayer structure is accompanied by the changes in interatomic distances [see Fig. 2(c)]. The bond lengths in the bilayer structures are generally smaller than those in the trilayer structures. For example, the average bond length in the bilayer structure of Co_{16a} is smaller than that of trilayer Co_{16b} by 0.02 Å. This change mainly comes from the shrinkage of the interlayer distance. Besides, the appearance of center atom is another difference between trilayer structure and bilayer structure.

The structural changes are clearly reflected in the DOS shown in Fig. 3. As can be seen, the DOSs of all four bilayer clusters, Co_{13}, Co_{14}, Co_{15}, and Co_{16a}, are very similar to each other. As the clusters adopt the trilayer structure from Co_{16b},

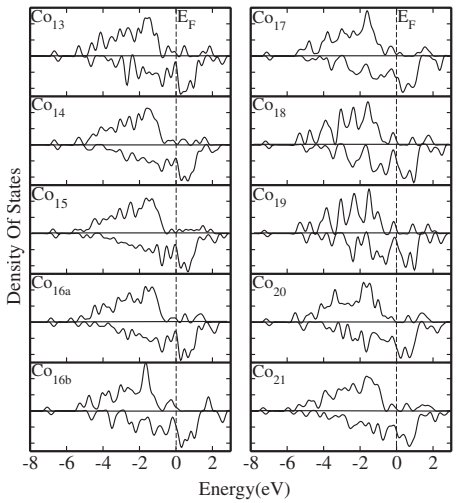

FIG. 3. Spin-polarized density of states of present layer-like structures. Apparent difference can be seen between Co_{16a} and Co_{16b}, as well as Co_{19} and Co_{20}.

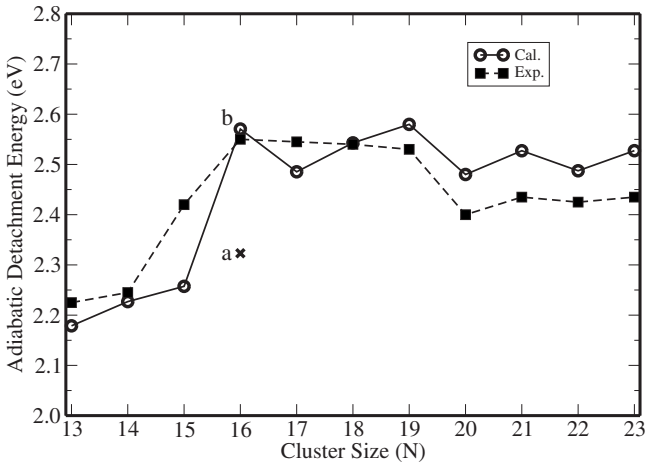

FIG. 4. Comparison of calculated ADEs with the experimental feature threshold. The solid square is for experimental data and the open circle for calculated ADE. Value for bilayer Co_{16a} is also presented (×).

the peaks become more and more sharply resolved, such as the peak around −1.6 eV in spin majority states, which is mostly of E_g character. This trend can be seen in both spin majority and minority states. When the cluster transforms to hcp-like, the peaks around −1.6 eV in DOS of Co_{20} and Co_{21} become broaden again. It is easy to understand why the DOSs of Co_{16b}–Co_{19} have sharper peaks. This is because they have high symmetry, in fact, Co_{19} is a perfect octahedron with an O_h symmetry.

In the PES, similar trend can be found.[26,40] The PES shows apparently different features in three neighboring size ranges, namely, $N=13-15$, $N=16-19$, and $N\geq 20$. These changes in PES indicate evidentially structural transitions, which surprisingly occur at exactly same sizes with the present theoretical results, namely, $N=16$ and 20. In fact, the experimental photoelectron spectra for Co_{16b}–Co_{19} have sharp peaks, indicating a high symmetry. However, due to the complexity of d electron, both the position and height of the peak between PES and DOS are not comparable.

We have also calculated the adiabatic detachment energy (ADE), which is the energy difference between the optimized anionic structure and its neutral counterpart. As ADE corresponds to the experimental onset threshold of PES, they are both shown in Fig. 4 for comparison.[40] The experimental data have an abrupt rise from $N=14$ to $N=16$ and decrease slightly for $N>19$. Both the values and variation of calculated ADE are in fairly good agreement with the experimental data. Moreover the Co_{16b} clearly with better agreement than Co_{16a} verifies again the bilayer to trilayer transition at $N=16$ for anionic structures.

One major aspect of interest in Co clusters is the magnetism and its evolution with size. Magnetic properties essentially depend on the electronic behavior, and the later has an important influence in the formation of atomic structure. To understand why the layer-like structures are stable, we have calculated the magnetic moments of both the layer-like and icosahedral-like structures, as shown in Fig. 5(a). With the geometry of these structures (optimized under spin polarization) fixed, we also performed spin-unpolarized calculation.

Figure 5(b) shows the magnetic energy, which is defined as the energy differences between results of spin-polarized and spin unpolarized calculation for both the layer-like and the icosahedra-like structures. Although the spin moment versus N curves for layer-like and icosahedra-like structures is similar in trend, the magnetic moment of layer-like Co clusters is typically much larger. It is interesting to note that the magnetic energy of the layer-like structures decreases with size increasing, while it does not show a monotonic behavior for the icosahedral-like structures (with a maximum at $N=18$). For the Co_{13}–Co_{17} clusters, magnetic energies for the layer-like structure are about 0.1 eV/atom larger than their icosahedral-like counterparts. For Co_{17} and larger clusters, magnetic energy difference gradually becomes negligible. To

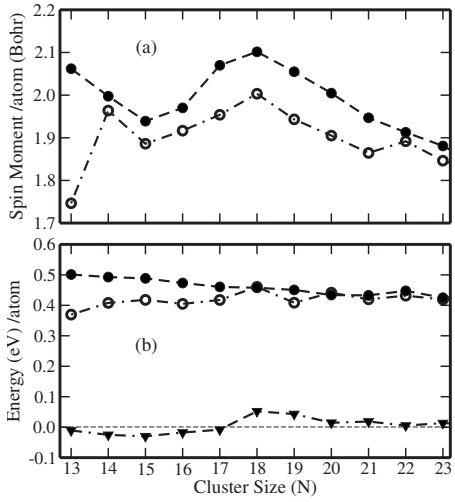

FIG. 5. (a) Spin moment of layer-like structure (solid dot) and their icosahedral-like counterparts (open circle). (b) Magnetic energy, calculated as the energy difference between the spin-polarized and spin-unpolarized calculations, of layer-like structure (solid dot) and their icosahedral counterparts (open circle). Moreover binding-energy difference of layer-like structures and their icosahedral-like counterparts obtained by spin-unpolarized calculation (triangle).

elucidate the rule of magnetization on the structural stability, we also calculated the binding-energy difference between the layer-like structure and icosahedral-like structure without spin polarization. As shown in Fig. 5(b), one can see that, without spin polarization, the icosahedral-like structures would prevail for the Co_{13} to Co_{16}. These analyses strongly suggest that stabilities of the layer-like structures are facilitated by the magnetism of the Co clusters.

In summary, we find a type of layer-like structures for Co_N ($N=13-23$) clusters, which are much more stable (by as much as ~0.6 eV in energy) than their icosahedron-like counterparts. The stability of the layer-like $Co_{13}-Co_{16}$ clusters stems from the enhanced magnetization. The critical sizes of phase transitions along the series of structures are in agreement with the sudden changes in PES features at $N=16$ and $N=19$. Since the kernels in all these clusters are small hexagonal planes, Co_N cluster might be another one that encompasses fragments of bulk lattice $N \leq 20$.

We are thankful to the discussions with L. S. Wang, D. S. Wang, R. Q. Wu, and X. F. Jin. This work was supported by the National Science Foundation of China, the special funds for major state basic research, Shanghai local support. The computation is performed at Fudan supercomputer center.

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