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Density Functional Theory Study on Structural and Magnetic Properties of Aluminum Cuboctahedral Clusters

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[INTRODUCTION]

Aluminum nanoclusters, which are metallic grains, play important roles in chemical reactions and nano-sized device with many chemical and physical properties such as catalysis, conductivity, superconductivity, magnetic properties and so on [1]. Enhanced stability against dissociation or fragmentation has been found in metallic clusters of particular size. These clusters are called "magic clusters" [2]. The common "magic numbers" of metallic clusters appear when the total number of atoms is 13, 55, 147 and so on. Martin *et al.* [3] showed that for large Al_n (n = 250-10 000) clusters, "magic numbers" were due to geometric closings associated with face-centered-cubic octahedral and this hypothesis is consistent with results of kinetic simulations [4].

The aim of present study is to investigate magnetic properties of cuboctahedral Al_n (n = 13, 55, 147, 309, 561, and 923) "magic clusters" by DFT calculations. We discuss the size dependence of binding energy and magnetization for these Al_n cuboctahedral clusters across the range of sizes. We focus on the distribution of electron, spin density in relation to shell structure.

[COMPUTATIONAL METHOD]

The DFT calculations in this study have been performed by using the Vienna Ab-initio Simulation Package (VASP) [5] with projector-augmented wave (PAW) potentials [6] to describe the electron-ion interaction. The spin-polarized calculations have been carried out in order to determine the magnetic ground state of the Al_n clusters within generalized gradient approximation (GGA) and the exchange-correlation functional are described by the Perdew-Wang (PW91). The periodic boundary conditions are applied and the isolated clusters are placed inside a very large cubic cell with size-length is 35Å, so the interaction between the clusters in neighboring cells to be negligible. Because of no dispersion in the space between clusters and the Bloch theorem does not apply, hence there is no need to use more than one single k-point, the integration over the Brillouin zone therefore is needed to be done approximately for the Γ-point only.

[RESULT AND DISCUSSION]

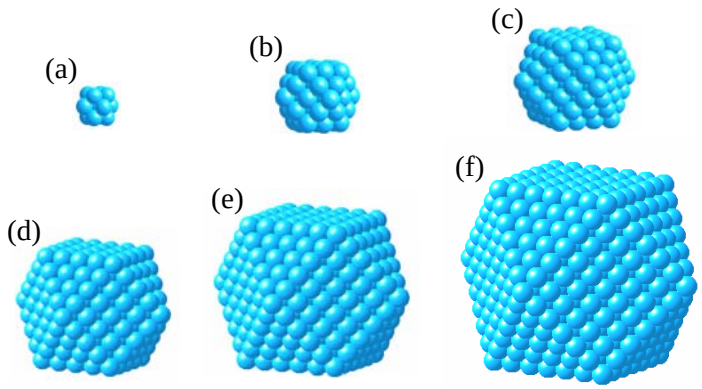

FIGURE 1. Representations of the geometrical structures with increasing the number of atoms: (a) Al_{13} (one centered atom and one shell), (b) Al_{55} (two shells), (c) Al_{147} (three shells), (d) Al_{309} (four shells), (e) Al_{561} (five shells) and (f) Al_{923} (six shells).

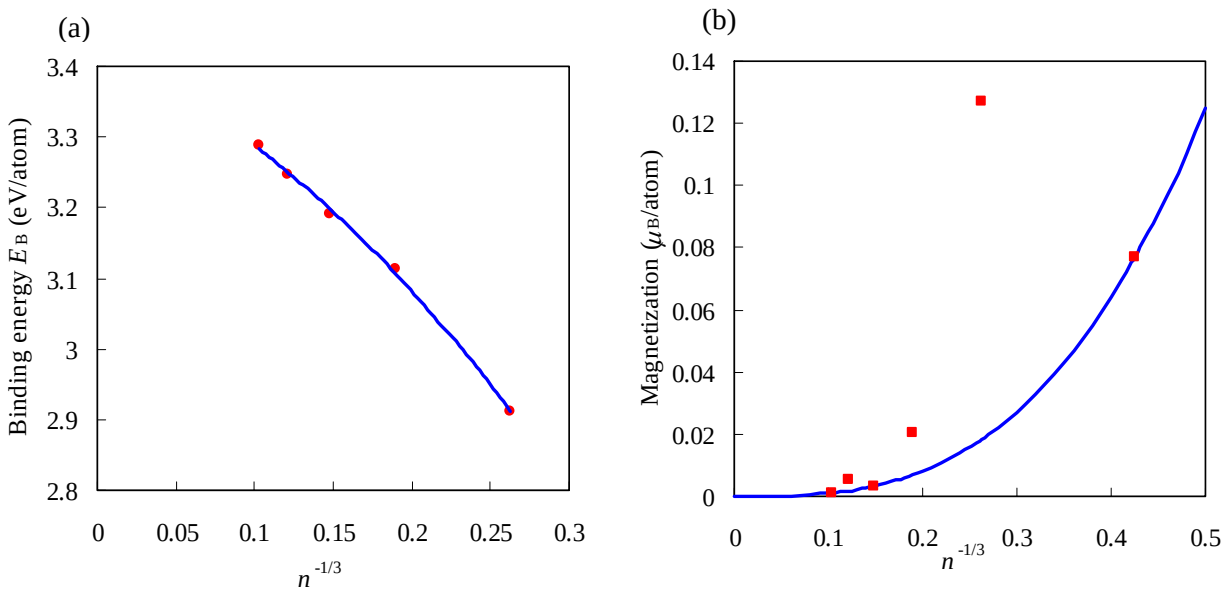

FIGURE 2. The size dependence of binding energy and magnetization for cuboctahedral Al_n (n = 13, 55, 147, 309, 561, 923) clusters. (a) Binding energy versus $n^{-1/3}$. (b) The size dependence of magnetization for Al_n clusters. The solid curve is function n^{-1}.

From the size dependence of binding energy of Al_n (n = 13, 55, 147, 309, 561, and 923) clusters as shown in Fig. 2 (a), we have estimated the coefficients corresponding to surface and edge energies for cuboctahedral Al_n clusters through the fitting function of size dependent binding energy.

$$E_B = E_0 + an^{-\frac{1}{3}} + bn^{-\frac{2}{3}}. \quad (1)$$

E_0 represents the cohesive energy, *i.e.* the bulk binding energy per atom; the a and b fitted coefficients correspond to the surface and edge energies, respectively. Our results have shown a = -0.9307, b = -3.7690. The cohesive energy of bulk system 3.418 eV is estimated, very close to experiment value (3.39 eV) [7].

The total number of electrons of cuboctahedral Al_n clusters is always *odd* because of *odd* number of atoms. We can expect that the total magnetization becomes:

$$\mu^{tot} \geq 1. \quad (2)$$

The spin magnetic moment per atom is reduced as the size of Al_n clusters increased, however, that does not occur smoothly with increasing cluster size as shown in Fig. 2 (b). Using the shell structure concept for cuboctahedral, the m^{th} shell consists of ($10m^2$ + 2) atoms, we analyzed the distribution of electron and spin density per atom in each shell. The distribution of magnetization shows the spin density is localized at the outmost shell. From Al_{309} to Al_{923} clusters, electrons in the center and inner most shell might be similar to the bulk.

In summary, we have investigated the dependence of the energetic stability and magnetization on the size of Aluminum cuboctahedral clusters by first-principle calculation. The magnetization in the outmost shell of Al_n cuboctahedral clusters is largest in all shells in these cluster size regions. The inner most shell and the centered atom approach to the bulk from Al_{309} cluster.

References

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