3E14

密度汎関数法を用いたアルミクラスタのイオン化ポテンシャルに関する理論的研究

Density Functional Theory Study on Ionization Potential of Aluminum Clusters

(Division of Mathematical and Physical Science, Graduate School of Natural Science and Technology, Kanazawa University)

○**Thi Viet Bac Phung, Taihei Hashimoto, Kyoshi Nishikawa and Hidemi Nagao**

[INTRODUCTION]

Nanosized systems have much interest in new characteristics arising from their discrete energy level, their properties have been investigated experimentally and theoretically from viewpoints of new chemical and physical phenomena. As metallic nanoclusters, aluminum clusters containing a few hundred atoms are expected to have strongly size-dependent properties such as the geometrical and electronic structures, binding energy, etc., and its properties smoothly tend to the bulk limit as its size increases. We have investigated the size dependence of magnetic properties of several small-sized and some cuboctahedral aluminum clusters. In this study, we discuss the size dependence of the ionization potential of aluminum clusters with numerical results in relation to theoretical models by Wood and Perdew. Next, we present new expressions of the higher order ionization potential based upon the Perdew model for the metallic clusters. Then the theoretical model based upon the Perdew model for the ionization potential is extended to a collective system of clusters. Finally, we discuss the superconductivity of aluminum clusters under consideration.

[COMPUTATIONAL METHOD]

The first-principle calculations were carried out in the framework of the density functional theory (DFT) [1] using the Vienna Ab-initio Simulation Package (VASP 4.6) with the plane wave basis set. The exchange-correlation functional was described within the generalized gradient approximation (GGA) in the formulation of Perdew and Wang (PW91). We have performed the full-potential projector-augmented wave (PAW) method implemented in VASP and the spin-polarized interpolation of the correlation part according to S. H. Vosko, L. Wilk and M. Nusair [2]. All plane-waves with a kinetic energy smaller than E_{cut} = 300 eV are included in the basis set. The simple cubic super-cells are used with the periodic boundary conditions (PBC), where we have chosen a cube of size 35Å×35Å×35Å which is large enough for the neighboring clusters to be kept separated by vacuum space and ensures that the interaction of clusters with their images is negligible. Reciprocal space integrations are carried out at the Γ-point only. Both corrections of dipole and quadrupole moments are calculated using methods discussed by G. Makov and M. C. Payne [3] and added to the total energy, so that these effects caused by the periodic boundary conditions are excluded to get well converged energy of both the neutral and charged clusters.

[RESULT AND DISCUSSION]

The results of the ionization potential and the electron affinity of Al_N (N = 2-17) clusters and cuboctahedral Al_N (N = 13, 55, 147, 309, 561, and 923) clusters obtained from DFT calculations are compared to those calculated through the above models. In Figure 1, we plotted the E_{IP}, E_{EA} [Fig. 1(a)], and the chemical hardness H [Fig. 1(b)], which depend on the cluster sizes $x=N^{-1/3}$. As shown in Figure 1(a), in general, the IP and cluster size increase in opposite directions.

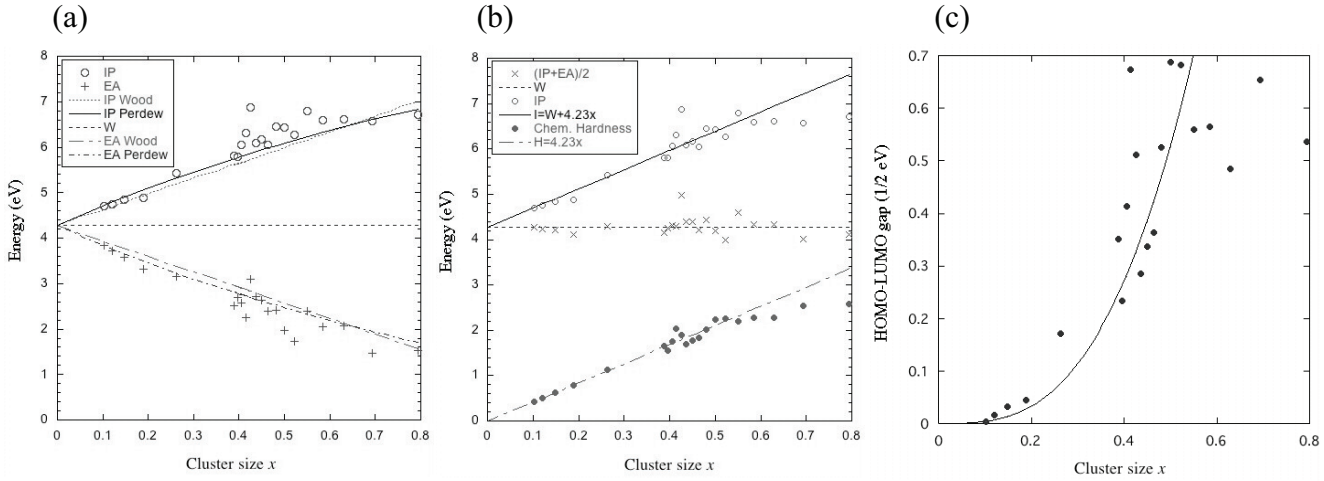

FIGURE 1. The size dependence of the ionization potential, electron affinity (a), chemical hardness (b), and HOMO-LUMO energy gap (c) of aluminum clusters. The work function W is displayed by the dashed line equal to 4.28 eV of the measured bulk work function. The cluster size is calculated by $x=N^{-1/3}$.

In the case of the spherical structures of the cuboctahedral aluminum clusters up to 923 atoms, the results of IP and EA show a very good agreement with the well-known predictions of Wood [4] and Perdew [5].

As the cluster size increased ($x \rightarrow 0$), the IP and IA show the tendency towards the bulk work function value of 4.28 eV. In general, the chemical hardness is smaller for larger clusters [see Fig. 1(b)], and the chemical hardness of the large cuboctahedral clusters is linearly dependent on the cluster size.

As the level spacing is increased, the superconducting gap of the grain vanishes at the critical value. In the present systems of the cuboctahedral aluminum clusters, the parity of the number of electrons in the system is odd size. The critical level spacing for superconductivity is

$$\delta\varepsilon_c^o = \frac{e^\gamma \Delta_o}{2} \approx 0.89\Delta_o \quad (1),$$

where Δ_0 means the superconducting gap of the bulk system (Δ_0= 0.31meV) and γ is Euler's constant. Therefore, $\delta\varepsilon^o_c$ can be estimated as 2.759 $\times 10^{-4}$ eV. From the size dependence of the HOMO-LUMO gap [Fig. 1(c)] and using the following approximation of chemical hardness

$$H = \frac{\varepsilon_H - \varepsilon_L}{2} + \frac{e^2}{2R_c} \quad (2),$$

we can approximately estimate the critical size for the superconductivity of the cuboctahedral aluminum cluster as N_c = 31,352. We obtained $R_c \approx 50$ Å as the radius of the critical size. This result suggests that in the case of the cluster diameter being smaller than 100 Å, the superconductivity may vanish. The critical particle size here agrees well with the size where destroy superconductivity in 0D aluminum superconductors given by M. Tinkham [6].

[References]

[1]. Kresse, G. and Joubert, J. *Phys. Rev. B* **59**, 1758 (1999).
[2]. Vosko, S. H et al. *Can. J. Phys* **58**, 1200 (1980).
[3]. G Makov and M. C. Payne. *Phys. Rev. B* **51**, 4014 (1995).
[4]. D. M. Wood. *Phys. Rev. Lett.* **46**, 749 (1981).
[5]. E. Engel and J. P. Perdew. *Phys. Rev. B* **43**, 1331 (1991).
[6]. M. Tinkham *J Superconductivity* **13**, 801 (2000).