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Ground State Structures of Neutral and Charged Ti Clusters Containing 2 to 16 Atoms^{*1}

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By using a simulated-annealing technique with a tight-binding molecular-dynamics, optimized structures of neutral and positively- and negatively-charged Ti clusters are determined for the number of atoms $n = 2-16$. It is found that the clusters with the sizes of $n = 7, 9, 13$ and 15 are specifically stable compared to those with the other sizes. These magic numbers agree well with the experimental results of time of flight mass spectrometry and collision induced dissociation with Xe. The physical origin of the magic numbers is discussed.

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Keywords: magic number, simulated annealing, binding energy, interatomic distance

1. Introduction

Transition metal clusters have attracted much attention for the past decade. In contrast with a number of studies on the other transition metal clusters, such as Fe, Ni, and Cu clusters, Ti clusters have not been studied so intensively. So far, however, two intriguing experimental results on the stability of Ti clusters have been reported. By using laser vaporization cluster source, Sakurai *et al.* have measured the time of flight (TOF) mass spectra for positively-charged Ti clusters with 2 to 28 atoms.¹⁾ In the mass spectra, they found specifically stable cluster sizes compared to the other cluster sizes, so-called magic numbers, $n = 7, 13, 15$, and 19 . Lian *et al.* have performed an experiment of collision induced dissociation (CID) of Ti_n^+ ($n = 2-22$) clusters with Xe and obtained specifically stable clusters at the sizes $n = 7, 13$, and 19 .²⁾ In general, the stable structures of the clusters are strongly related to its stability. Usually, first-principles molecular-dynamics calculations have been performed to determine the stable structures of clusters. Although this approach is the most reliable one in the methods we can use, application of the first-principles methods has been restricted to small systems since it is quite time-consuming. In the present study, we perform a tight-binding (TB) molecular-dynamics (MD) and a self-consistent tight-binding (SCTB) MD to determine the stable structures of neutral and positively- and negatively-charged Ti clusters. This method can calculate interatomic forces on the basis of electronic structure, and is much more efficient compared to the first-principles methods. By investigating the obtained results, we will discuss on the stability of Ti clusters in detail.

2. Computational Model

The TB parameters we use in the present study are an orthogonal version of those proposed by Mehl and Papaconstantopoulos.^{3,4)} We determine the TB parameters by fitting

to the first-principles results in which the cohesive energies and the eigenvalues of bcc, fcc, and sc titanium with several lattice constants around equilibrium points are included. The first-principles calculations have been done by using the package code of full linearized augmented plane wave (FLAPW) method, WIEN95.⁵⁾ To perform structure optimization of the clusters efficiently, we divide the optimization process into two steps. First, we perform a simulated-annealing (SA) calculations⁶⁾ of the neutral clusters with TB. Annealing of the clusters is started from randomly generated 16 initial structures for each cluster size. In TB, the on-site energies and the hopping integrals have functional forms as follows:

$$h_{i\eta} = a_{\eta} + b_{\eta}\rho_i^{2/3} + c_{\eta}\rho_i^{4/3},$$

$$\rho_i = \sum_{j \neq i} \exp(-v^2 R_{ij}), \quad (1)$$

$$P_{ij\kappa} = e_{\kappa} \exp(-g_{\kappa}^2 R_{ij}), \quad (2)$$

where $h_{i\eta}$ is the on-site energy of the orbital η ($=3d, 4s$, or $4p$) on atom i , and $P_{ij\kappa}$ is the hopping integral between atom i and j , where κ stands for the type of interaction (*e.g.*, $ss\sigma$, $pp\pi$, *etc.*). By diagonalizing the Hamiltonian matrix, one can obtain the eigenvalues and the eigenstates of the system. The total-energy of the present TB is expressed as,

$$E_{\text{tot}}^{\text{TB}} = \sum_{\lambda}^{\text{occ.}} \epsilon_{\lambda} f_{\lambda}, \quad (3)$$

where λ is the index for the eigenstate, and ϵ_{λ} and f_{λ} are the eigenvalue and the occupation number of the eigenstate, respectively.³⁾ By differentiating eq. (3) with respect to atomic positions, the interatomic forces (Hellmann-Feynman forces) can be derived analytically.

In the second step of the structure optimization, we carry out structure relaxation with self-consistent tight-binding molecular-dynamics (SCTB-MD). In this procedure, the stable structures are determined for neutral and positively- and negatively-charged Ti clusters. The initial structures for the structure relaxation are taken from the optimized structures obtained at the first step. In the present SCTB, the total-energy is written as follows:⁷⁾

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$$E_{\text{tot}}^{\text{SCTB}} = \sum_{\lambda}^{\text{occupied}} \sum_{\alpha, \beta} f_{\lambda} C_{\alpha}^{\lambda*} H_{\alpha\beta}^{\text{TB}} C_{\beta}^{\lambda} + \sum_{i,j} \Delta q_i \Delta q_j \gamma_{ij},$$

$$\Delta q_i = q_i - q_0, \quad \gamma_{ij} = \left(R_{ij}^2 + \frac{1}{U^2} \right)^{-1/2}, \quad (4)$$

where $C_{\alpha}^{\lambda*}$ and C_{β}^{λ} are the eigenvectors, $H_{\alpha\beta}^{\text{TB}}$ is the Hamiltonian matrix element of TB, q_i and q_0 are the number of electrons on site i and isolated neutral Ti atom, respectively. R_{ij} is the interatomic distance between site i and j , and U is the Hubbard parameter. One can calculate the total energy in SCTB by solving eq. (4) self-consistently. In SCTB, charge transfer effects are approximately included by the point charges on each atomic position. As we can see from eq. (4), γ_{ij} becomes equal to the Hubbard parameter when $R_{ij} = 0$. This means that the interaction between the electrons located on the same atom is included by using the Hubbard parameter. On the other hand, γ_{ij} becomes the Coulomb potential when $R_{ij} \rightarrow \infty$. Hence these two limits of the interaction between electrons are continuously interpolated via γ_{ij} . It is not difficult to differentiate eq. (4) analytically with respect to atomic positions, hence exact interatomic forces can be obtained. In both TB-MD and SCTB-MD, atomic positions are updated by the velocity Verlet algorithm where 1 MD time step is taken as 2 fs.

3. Results and Discussion

In Figs. 1 and 2, the total energy curves calculated by the present TB and the first-principles method (FLAPW) are shown. The TB parameters used in the present study are tab-

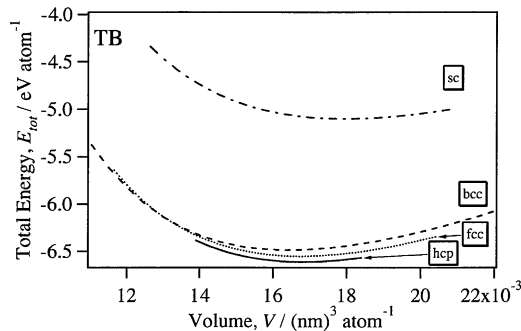


Fig. 1 Total energies calculated by the present TB as a function of volume.

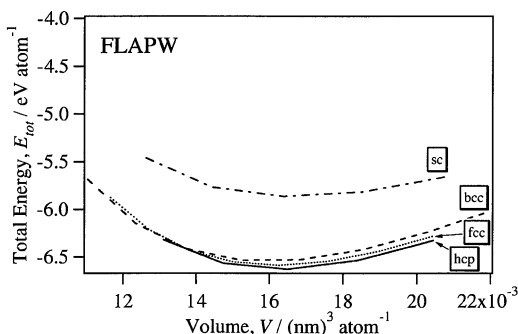


Fig. 2 Total energies calculated by FLAPW as a function of volume.

ulated in Tables 1 and 2. From the figures, it can be seen that the present TB reproduces the results of FLAPW very well. Especially, though hcp structures are not included in the fitting data, the present TB can correctly reproduce hcp phase as the ground state structure. This result indicates that the present model is transferable. Another transferability test of the model is application to Ti dimer. The equilibrium bond length and the binding energy of Ti dimer calculated by the present TB model are 0.209 nm and 2.58 eV, respectively. These results are in good agreement with the first-principles results: 0.183 nm and 2.60 eV, where the first-principles calculation is performed using the package program Gaussian94 (3-21G basis set, Slater exchange and Vosko-Wilk-Nusair correlation are used for calculation of singlet Ti dimer).⁸⁾

In Fig. 3, cluster size dependence of the binding-energies is shown for neutral and positively- and negatively-charged Ti clusters. From the figure, it is obvious that $n = 7, 9, 13,$ and 15 are more stable than the other clusters in both neutral and charged clusters. These magic numbers agree well with the experimental results of the TOF mass spectrometry and the CID. In the TOF mass spectra measured by Sakurai *et al.*, it was pointed out that $n = 7, 13,$ and 15 are magic numbers. Though Sakurai *et al.* did not count $n = 9$ in the magic numbers, a small peak at $n = 9$ can be recognized in the TOF mass spectra. Lian *et al.* pointed out that there are local maxima (these correspond to stable clusters) at $n = 7$ and 13 and local minima (these correspond to unstable clusters) at $n = 8$ and 14 in the cluster size dependence of the bond energies. Although Lian *et al.* did not mention that $n = 9$ and 15 are magic numbers, small peaks at $n = 9$ and 15 are recognized in the cluster size dependence of bond energies. Additionally,

Table 1 TB parameters for the on-site energies. $\nu = 1.20431295581$ (dimensionless), $R_c = 15.5$ (Bohr), $l = 0.3$ (Bohr), and $U = 6.74$ (eV). Definition of the parameters is described in eq. (1). In the present TB parameters, Bohr and Ry are used for units of distance and energy, respectively, where 1 Ry ≈ 13.605698 eV, 1 Bohr $\approx 5.29177249 \times 10^{-2}$ nm.

η	a_{η} (Ry)	b_{η} (Ry)	c_{η} (Ry)
3d	1.25291×10^{-2}	2.86101	12.7550
4s	-1.25291×10^{-2}	20.2887	1.05875×10^2
4p	1.63076×10^{-1}	25.8465	-90.3919

Table 2 TB parameters for the hopping integrals. Definition of the parameters is described in eq. (2). Interaction type κ is in accordance with conventional notation.

κ	e_{κ} (Ry)	g_{κ} (dimensionless)
ss σ	-2.88030×10^{-1}	5.94557×10^{-1}
pp σ	3.63126	7.40257×10^{-1}
pp π	-2.80335×10^{-2}	7.40257×10^{-1}
dd σ	-2.55568	8.34218×10^{-1}
dd π	1.65531	8.34218×10^{-1}
dd δ	-2.73858×10^{-1}	8.34218×10^{-1}
sps σ	1.80243	7.12926×10^{-1}
sds σ	5.30998×10^{-1}	6.78375×10^{-1}
pds σ	1.34026	7.27931×10^{-1}
pds π	-3.50095×10^{-1}	7.27931×10^{-1}

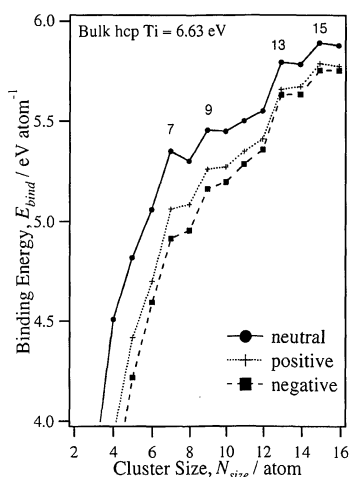


Fig. 3 Cluster size dependence of the binding-energy of neutral and charged Ti_n clusters ($n = 2-16$).

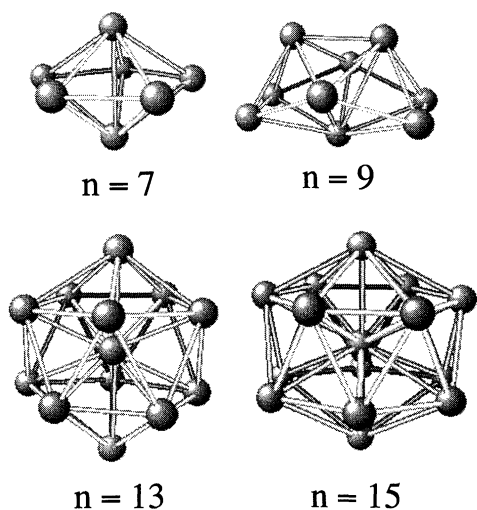


Fig. 4 Stable structures of neutral Ti_n clusters ($n = 7, 9, 13$, and 15).

since the clusters with the sizes neighboring to local minima become relatively stable compared to the other sizes, it is reasonable to include the cluster sizes of $n = n_{\text{minima}} \pm 1$ in the magic numbers (where n_{minima} is the cluster size of the local minima). Therefore $n = 9$ and 15 may also be counted in the magic numbers ($n = 7$ and 13 are already included). As a result, the experimental magic numbers concluded from both the TOF mass spectrometry of Sakurai *et al.* and the CID of Lian *et al.* are $n = 7, 9, 13$, and 15 . These summarized experimental magic numbers show exact agreement with the present ones.

Figure 4 shows the stable structures of magic number clusters Ti_n ($n = 7, 9, 13$, and 15). It can be seen from Fig. 4 that Ti_7 is a pentagonal bipyramid and Ti_9 has the shape of double pentagonal bipyramid. Ti_{13} is an icosahedral cluster, and Ti_{15} has a spherical structure with six-fold rotational symmetry. In the cluster size range of $n = 2-14$, Ti clusters show a growth on the basis of an icosahedral regime. Lian *et al.* discussed about the structures of the Ti clusters in Ref. 2). In their discussion, it was described that Ti_7 and Ti_{13} could have

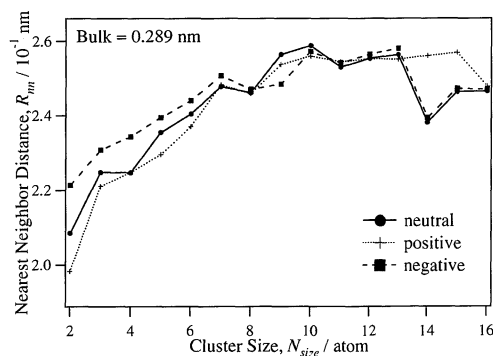


Fig. 5 Cluster size dependence of the nearest-neighbor distances of neutral and charged Ti_n clusters ($n = 2-16$).

icosahedral structures similar to those found in the present study.

Usually, the magic numbers of clusters are due to geometric or electronic shell effect. In the present study, the magic numbers of charged clusters are similar to those of neutral clusters. If electronic shell effect dominates the bonding of Ti clusters, the difference in the total number of valence electrons ought to change the magic numbers as we can see in the case of Cu clusters.¹⁰⁾ These results indicate that the stability of Ti clusters is not so affected by the total number of electrons, therefore we can say that electronic shell effect is not recognized in the magic numbers of Ti_2-Ti_{16} . Additionally, by checking the HOMO-LUMO energy gaps of Ti_n , we confirm that large HOMO-LUMO gaps are not found at the sizes $n = 7, 9, 13$, and 15 compared to the other sizes. From these results and the fact that the stable clusters obtained in the present study have geometrically closed structures, it is concluded that the extraordinary stability in Ti_n clusters at $n = 7, 9, 13$, and 15 is ascribed to geometric shell effect.

Nearest-neighbor distance is one of the important parameters reflecting the structures of clusters. Figure 5 shows cluster size dependence of the nearest-neighbor distances of neutral and charged Ti clusters. In the present study, the first peaks in the pair distribution functions are adopted as the nearest-neighbor distances. The pair distribution functions are generated by the Gaussian broadening with a width of 5.3×10^{-3} nm. As we can see from Fig. 5, compared to those of the neutral clusters, the nearest-neighbor distances decrease and increase in the positively- and negatively-charged clusters of $n = 2-8$, respectively. These changes in the nearest-neighbor distances can be understood from the viewpoint of molecular-orbitals (MOs). Generally, the MOs of clusters are classified into bonding orbitals and anti-bonding orbitals. When the number of anti-bonding electrons decreases or the number of bonding electrons increase, the bonding becomes stronger, which decreases the nearest-neighbor distance of the cluster. On the other hand, when the number of anti-bonding electrons increases or the number of bonding electrons decreases, the bonding becomes weaker, which increases the nearest-neighbor distance. In accordance with MOs analysis mentioned above, the HOMO and LUMO of neutral Ti clusters smaller than $n = 9$ are anti-bonding orbitals.

The largest cluster investigated in the present study shows

still smaller distance compared to that of bulk hcp Ti. To study the cluster-bulk transition appear in the ground state structures, it is necessary to explore larger clusters than those of the present study. For this purpose, structure optimizations of Ti clusters containing 55 to several hundreds atoms are currently in progress.

4. Summary

By performing the simulated-annealing with TB-MD and SCTB-MD, we determined the ground state structures of neutral and charged Ti_2 – Ti_{16} . Ti clusters show the growth in accordance with icosahedral regime. It was found that Ti_7 , Ti_9 , Ti_{13} and Ti_{15} are specifically stable compared to the other clusters. The magic numbers of Ti clusters are due to geometric shell effect. Charge effect appears as changes of the nearest-neighbor distances. Positive- and negative-charge induce contraction and expansion of Ti_2 – Ti_8 clusters, respectively. These changes are ascribed to the anti-bonding HOMO and LUMO of the neutral Ti clusters. The nearest-neighbor distances show contraction compared to that of bulk hcp Ti. Even in the largest cluster in the present study, the nearest-neighbor distance does not reach the bulk value.

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