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LETTER TO THE EDITOR

Stable disordered structures of vanadium clusters

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Abstract

Tight-binding and self-consistent tight-binding molecular dynamics are performed to determine the stable structures of V_n ($n = 2$–17, 55, 147 and 309). The globally optimized structures of V_2–V_9 are in good agreement with first-principles results. For V_{15}–V_{309}, amorphous-like disordered structures are found. The stability of the disordered clusters are discussed from the viewpoint of the local energy distribution in V_{55}.

So far, many researchers have studied the magnetism [1], electronic structures [2, 3], and energetics of V clusters [4]. Despite the fruitful results of these studies, knowledge of the ground-state structures of vanadium clusters, particularly those greater than 10 atoms, is still scarce. In theoretical studies, the stable structures of transition metal clusters with a large number of atoms have usually been determined with classical potentials, such as the Sutton–Chen potential and the Gupta potential [5]. While the molecular-dynamics (MD) simulations with classical potentials are so efficient that they are suitable for large-scale systems, the potentials are less reliable than more sophisticated electronic-structure calculations. To refine the results of a classical MD, a first-principles MD has been applied to re-optimize the clusters optimized with a classical MD. Recently, using this combined approach, a new class of stable structures of transition metal clusters, i.e. amorphous-like disordered clusters, has been found and studied [6, 7].

In the present letter, we will report on globally optimized structures of V_2–V_{17} and locally optimized ones for V_n ($n = 13, 55, 147$ and 309) determined by a tight-binding MD (TB-MD). TB-MD is an electronic-structure calculation method that employs parametrized Hamiltonian matrix elements, and is more efficient than first-principles methods. Additionally, a self-consistent TB-MD (SCTB-MD) was also carried out to optimize V_2–V_{17} locally. SCTB-MD takes account of charge-transfer effects in order to avoid unphysical large-charge transfer which can occur in the non-SC TB calculations of small clusters [8]. While the calculation time required for SCTB-MD is usually several times as long as that of TB-MD, SCTB-MD can yield more reliable results. TB-MD and SCTB-MD have successfully been applied to studying bulks, surfaces and clusters (see [11]).

The TB parameters we used are an orthogonal version of those proposed by Mehl and Papaconstantopoulos [9]. We determined the TB parameters by fitting to the first-principles

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results (the cohesive energies and the eigenvalues of bcc and fcc V with several lattice constants around the equilibrium points). In the fitting procedure a total of 11 355 eigenvalues and 15 cohesive energies were fitted by adjusting 25 independent TB parameters. The first-principles calculations were carried out with a package code of the full linearized augmented plane wave (FLAPW) method, WIEN95 [10]. The TB parameters we determined are summarized in tables 1 and 2. In TB, the on-site energies and the hopping integrals are expressed by

$$h_{i\eta} = a_\eta + b_\eta \rho_i^{2/3} + c_\eta \rho_i^{4/3} \qquad \rho_i = \sum_{j\neq i} \exp(-\nu^2 R_{ij}) F_{\mathrm{c}}(R_{ij}) \tag{1}$$

$$P_{ij\kappa} = e_\kappa \exp(-g_\kappa^2 R_{ij}) F_{\mathrm{c}}(R_{ij}). \tag{2}$$

Where $h_{i\eta}$ is the on-site energy of the orbital $\eta(=$ 3d, 4s, or 4p) on atom i, $P_{ij\kappa}$ is the hopping integral between atom i and j, and κ stands for the type of interactions (e.g. $ss\sigma$, $pp\pi$). R_{ij} is the inter-atomic distance between site i and j, and $F_{\mathrm{c}}(R_{ij})$ is a cut-off function with a radius 14.5 Bohr. The total-energy of our TB is expressed by

$$E_{\mathrm{tot}}^{\mathrm{TB}} = \sum_{\lambda}^{occ} \epsilon_\lambda f_\lambda \tag{3}$$

where λ is the index for the eigenstate, and ϵ_λ and f_λ are the eigenvalue and the occupation number, respectively [9].

Table 1. TB parameters for the on-site energies. $\nu = 1.25$ (dimensionless).

η	a_η (Ry)	b_η (Ry)	c_η (Ry)
4s	−0.0166298	31.7880	113.710
4p	0.243447	23.2546	−41.8081
3d	0.0110865	1.91257	19.2677

Table 2. TB parameters for the hopping integrals. Interaction type κ is in accordance with conventional notation. g_κ is dimensionless.

κ	e_κ (Ry)	g_κ
ssσ	−0.991210	0.720205
ppσ	2.61092	0.729646
ppπ	−0.304966	0.729646
ddσ	2.28578	0.763098
ddπ	−3.47369	0.896783
ddδ	2.36459	0.896783
spσ	−0.510852	0.896783
sdσ	0.461023	0.757618
pdσ	0.623488	0.663583
pdπ	−0.219195	0.663583

In SCTB-MD, the total-energy is written as follows [11]:

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

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

Where $C_\alpha^{\lambda *}$ and C_β^λ are the eigenvectors, $H_{\alpha\beta}^{\mathrm{TB}}$ is the Hamiltonian matrix element of TB, q_i and q_0 are the number of electrons on site i and V atom, respectively. U is the Hubbard parameter (for V, $U = 3.1$ eV [12]). One can calculate the total-energy of SCTB by solving equation (4) self-consistently. In SCTB, charge-transfer effect is taken into account through the point charges on each atomic position. By differentiating equations (3) and (4) with respect to atomic positions, the inter-atomic forces (Hellmann–Feynman forces) can be derived analytically.

To determine efficiently the global minimum structures of V_2–V_{17}, we divided the optimization procedure into two steps. In the first step, simulated-annealing (SA) calculations were performed with TB-MD. As the initial structures in the SA runs, randomly generated structures (from 16 to 32 samples at each cluster size) were used. In the second step of the structure optimization, we quenched with SCTB-MD the stable clusters obtained in the first step.

Figure 1 shows the volume dependence of the total energies calculated by TB and FLAPW. The band structures for bcc V by these two methods are plotted in figure 2. From the figures, it can be seen that TB reproduces the results of FLAPW very well. It is noted that TB can correctly reproduce the total energies of the hcp phase, though hcp structures were not included in the fitting data. This result indicates that our TB is transferable. Another transferability test is an application to V dimer. The equilibrium bond length of V dimer calculated by the present TB is 1.76 Å. This result is in good agreement with first-principles results, 1.69–1.86 Å [13] and 1.75–1.79 Å [14], and an experimental result, 1.77 Å [15]. In contrast to the good agreement between the bond lengths, the binding-energy we obtained for the dimer was larger than the experimental value by about 2 eV. This is mainly due to the underestimation of the atomic total energy in the local density approximation. This situation was similar in the larger clusters and bulk crystals.

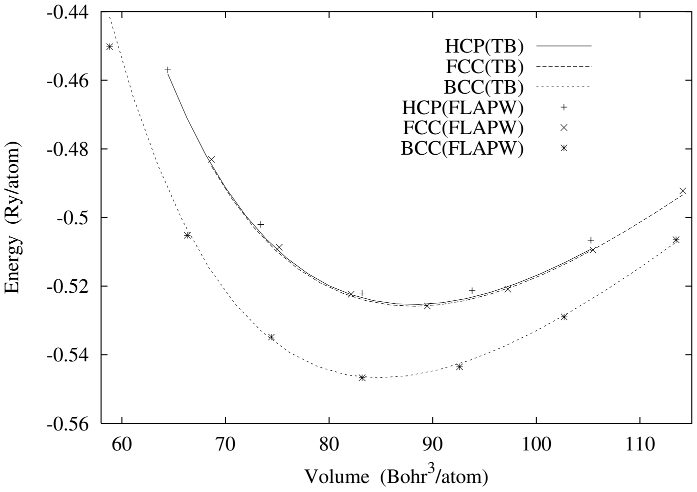

Figure 1. Total energies calculated by TB and FLAPW as a function of volume.

In figure 3, the most stable structures we obtained are shown in a size range of 3 to 17 atoms. V_3 was a isosceles triangle with an apex angle of 64.1° and a long-side bond length of 2.06 Å; these values are very close to the first-principles result, 65.91° and 2.144 Å, obtained by Wu and Ray [13]. V_4 was a tetrahedron with a bond length of 2.19 Å. There are two first-principles results for V_4, whereas they are inconsistent: Wu and Ray obtained a tetrahedron with a bond

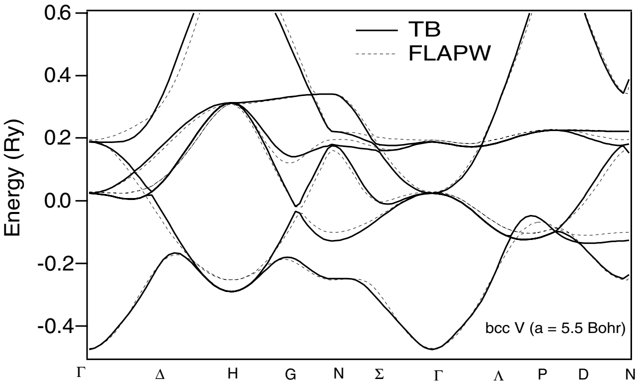

Figure 2. Band structures for bcc V with a lattice constant 5.5 Bohr by TB and FLAPW. Fermi energy is set to zero.

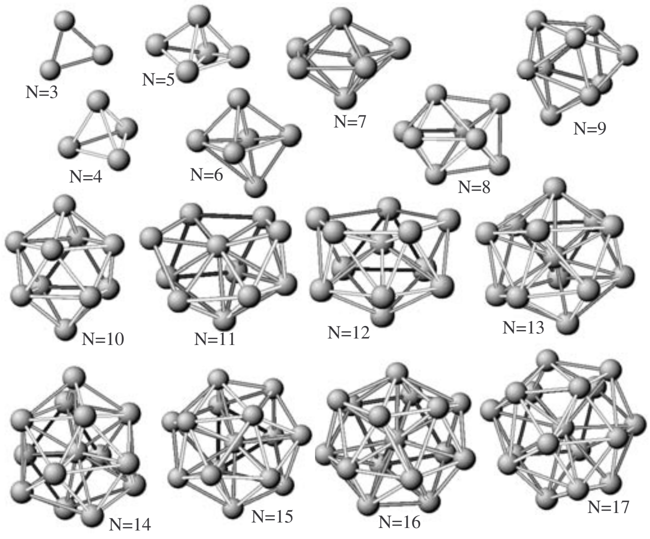

Figure 3. The most stable structures of V_3–V_{17}.

length of 2.206 Å [13], which is in good agreement with the present results, whereas Grönbeck and Rosén obtained a planar structure as the ground state of V_4 [14]. In our results any planar structure was not obtained for optimized V_4. V_5 was a distorted trigonal bi-pyramid with the C_{2V} symmetry in agreement with the first-principles results by Wu and Ray [13]. In their results, two of the bond lengths of the trigonal bi-pyramid are 2.194 Å and 2.344 Å [13]; the corresponding values we obtained were 2.15 Å and 2.22 Å, respectively. The hexamer was a heavily distorted octahedron. A similar structure was found to be the lowest-energy isomer of V_6 by Grönbeck and Rosén [14]. The most stable structure of V_7 and V_8 are a distorted pentagonal bi-pyramid and a bi-capped distorted octahedron, respectively. These structures also agree with the first-principles results, that for V_7 by Grönbeck and Rosén [14] and that for V_8 by Wu and Ray [13]. In the present results, it was found that V_9 has a tri-capped prism structure. This structure is included in the lowest-energy isomers found by Wu and Ray [13].

Thus, the most stable structures of V_2–V_9 we obtained are in good agreement with those of first-principles studies.

V_{10} has a structure with the D_{4d} symmetry. The stable structures of V_{11} and V_{12} are a part of a distorted icosahedral cluster which is the most stable structure of V_{13}. V_{14} has a structure similar to heavily distorted V_{13} with one adatom. As can be seen from figure 3, V_{15}–V_{17} are spherical clusters with disordered structures. Recently, the potential energy surface (PES) of the metal clusters containing six to 75 atoms have intensively been investigated using Gupta potential by Michaelian *et al* [5]. They found that Ni and Ag clusters have disordered local minimum structures, and the ground-state structures of Au clusters are disordered ones. In a density functional study of Pt_{13}, Yang *et al* have also found amorphous-like disordered structures in the lowest-energy isomers [16]. These many discoveries of stable-disordered structures imply that disordered structure is one of the main structures of metal clusters, such as icosahedral and cuboctahedral structures.

As is well known, it is quite difficult to determine the ground-state structures of large clusters, since the number of local minima rises exponentially with the number of atoms. For this reason, local optimization from given initial structures were used to obtain the stable structures of large V clusters. Initial structures used are the Mackay icosahedra and cuboctahedra with 13, 55, 147 and 309 atoms and an octahedron containing 209 atoms with bcc lattice. The nearest-neighbour distances of these initial clusters were set to be between 4.5–4.7 Bohr. Figure 4 shows the binding energies of V_{13}–V_{309} as a function of $n^{-1/3}$, where n is the number of atoms. From the figure, it can clearly be seen that the structures optimized from icosahedra (labelled DIS) are most stable in the size range. In figure 5, the most stable structure of V_{55} is shown. As can be seen from the figure, the stable V_{55} has a disordered structure, while there remains icosahedral features. For V_{13}, V_{147} and V_{309}, similar disordered structures were obtained as the most stable structures. To see the disordered structure more clearly, the atomic distribution from the centre of mass (ADCM) for V_{55} is plotted in figure 6. In the figure, the ADCM of the V_{55} relaxed from an icosahedron (labelled DIS) and a cuboctahedron with a fcc lattice (labelled FCC) are shown. As can be seen from the figure, the ADCM of the fcc V_{55} is stepwise because of the symmetry of a fcc lattice. The ADCM of fcc V_{55} is classified into five types: the atom assigned index 1 is the first shell (a central atom); those of index 2–13 belong

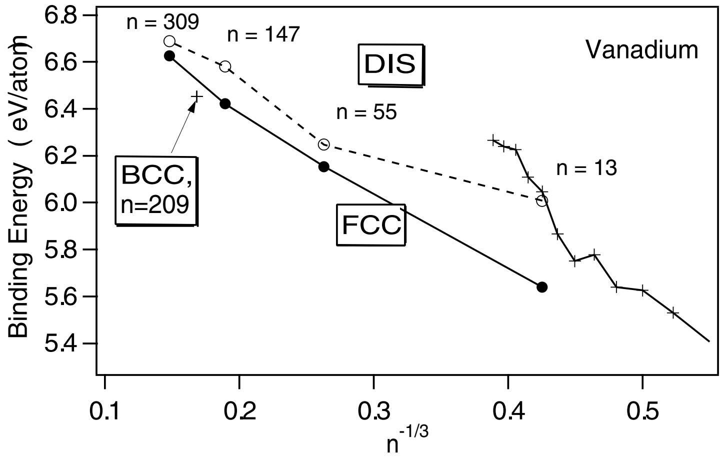

Figure 4. Binding energies for V_{13}–V_{309} with disordered, fcc, and bcc structures (labelled DIS, FCC, and BCC, respectively). Binding energies for small V clusters are also plotted (denoted by +).

to the second shell; index 14–19, 20–43 and 44–55 correspond to surface atoms; the last 12 atoms (index 44–55) are at vertices. The ADCM labelled DIS can be classified into three types (index 1, index 2–14 and index 15–55), which implies that the disordered V_{55} remained a geometric shell structure similar to that of the icosahedral cluster with 55 atoms. In contrast to fcc V_{55}, the V_{55} relaxed from an icosahedron has not a stepwise but a smooth-sloped ADCM for the surface atoms (index 15–55), this indicating that the surface structure is disordered.

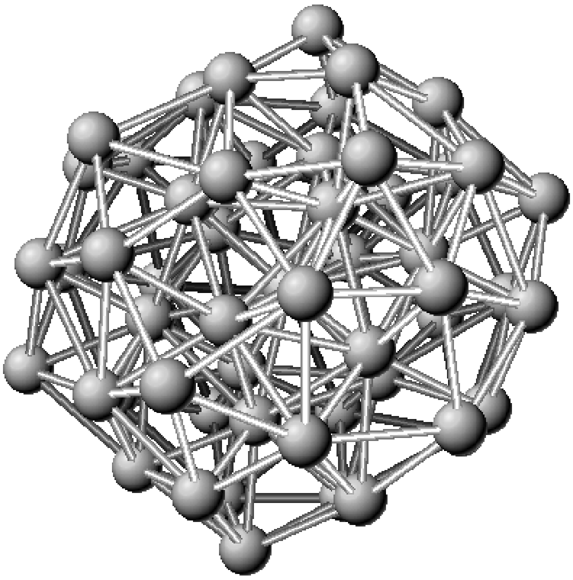

Figure 5. Stable structure of V_{55}.

Why are disordered structures more stable than the ordered icosahedral and cuboctahedral structures in vanadium clusters? Using Morse pair-potential, Doye and Wales have showed that disordered structures are the global minima for the clusters when the potential well is sufficiently wide [17]. By partitioning the potential energy of the cluster into the strain energy and the other energies, they found that the elastic energy plays an important role in the stabilization of the disordered structures. Soler *et al* have performed an exhaustive search for low-energy isomers of Au clusters with Gupta potential, and obtained many disordered clusters [7]. In particular, they found that the global minima of Au clusters with 19, 38 and 55 atoms are amorphous-like disordered ones. To study the origin of the stability of the disordered clusters, they examined the 'atomic energy' of disordered and icosahedral Au clusters, and found that most of the energy gain occurs in the central part of the clusters. In the present TB, the atomic energy E_i^{local} is expressed by

$$E_i^{\text{local}} = \sum_{\alpha\in i}\sum_{\lambda} \varepsilon_\lambda f_\lambda \left|C_{i\alpha}^{\lambda}\right|^2. \tag{5}$$

Where the sum of E_i^{local} over all atoms is equal to the total energy. The atomic energies for the disordered and fcc V_{55} are plotted in figure 7. From the figure, it can be seen that most of E_i^{local} labelled DIS are lower than those labelled FCC in the region of index 1–13. This implies that in the central part the disordered clusters have a crucially lower energy than icosahedral ones, because the central part of fcc clusters usually has lower energy than that of icosahedral ones.

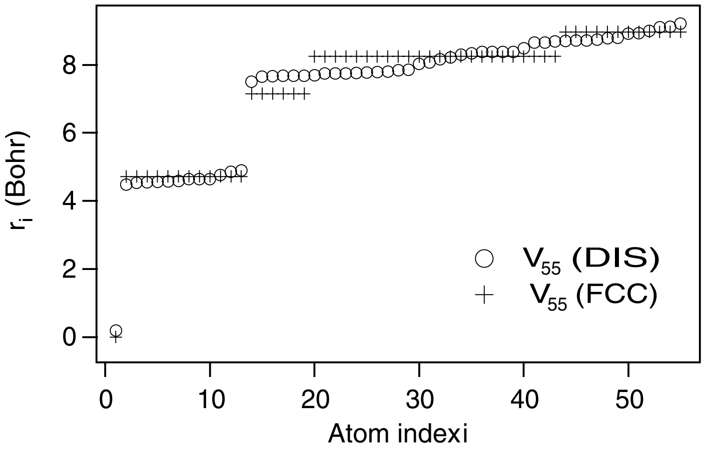

Figure 6. Atomic distribution from the centre of mass in V_{55} with a disordered (DIS) and a fcc (FCC) structure. r_i stands for the distance from the centre of mass. Atom indices are assigned in accordance with the distance from the centre of mass. (e.g. atom index 1 corresponds to a central atom and index 55 corresponds to a vertex atom).

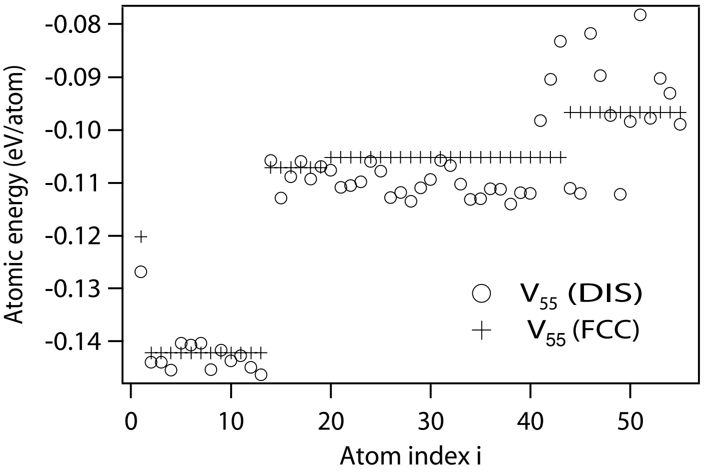

Figure 7. Atomic energy distribution in V_{55} with a disordered (labelled DIS) and fcc (labelled FCC) structure. Atom indices are same as those used in figure 6.

Therefore, it can be said that amorphous-like disordered vanadium clusters are also stabilized by the energy gain in the central part similar to those of Au clusters. Soler *et al* examined why the disordered structures are energetically favoured in Au clusters and found that gold has a small energy cost with respect to the disorder in co-ordination number and the change in bond-length [7]. Based on these two properties, they predicted the amorphization tendency for many elements, and the elements of group 5 (V and Nb) have relatively high tendency to amorphization. The prediction by Soler *et al* is in agreement with the present results.

Whereas the present results indicate the existence of the disordered V clusters up to 309 atoms (about 2 nm in diameter) at the ground state, there is no experimental evidence. However, x-ray diffraction experiments have been performed on the V clusters with a diameter larger than 10 nm prepared at a high cooling rate [18]. In the experiment, Kim *et al* measured x-ray diffraction spectra for the clusters and found that V clusters with a diameter smaller than 40 nm have disordered structures. This result is consistent with those we obtained.

In summary, TB-MD and SCTB-MD were performed to study the ground-state structures of V_2–V_{17} and locally optimized structures of $V_n (n = 13, 55, 147, 309)$ with the TB parameters determined on the basis of first-principles data. The optimized structures of V_2–V_9 were in good agreement with those by first-principles calculations. For V_{15}–V_{17}, disordered structures were found to be the global minima. In local optimizations, the icosahedral $V_n (n =13, 55, 147, 309)$ relaxed into disordered ones with no activation barrier and they are more stable than the ordered structures. The local structure and energetics of disordered V_{55} were investigated, and it was found that disordered structures are stabilized due to the energy gain in the central part of the clusters similar to those of Au clusters.

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Bibilography

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