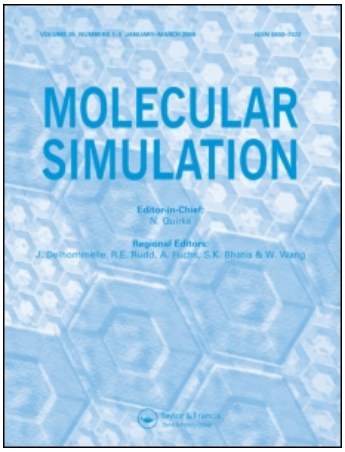

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First-Principles Molecular Dynamics Simulations for Se_8 and Se_8 Clusters

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FIRST-PRINCIPLES MOLECULAR DYNAMICS SIMULATIONS FOR Se_8 AND Se_8^+ CLUSTERS

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We have applied the first-principles molecular dynamics simulation based on the linearized-augmented-plane-wave (LAPW) method to Se_8 and Se_8^+ clusters. The equilibrium structures are obtained for Se_8 and Se_8^+ clusters: for the ionized cluster Se_8^+, we have found a remarkable structural change from that for the neutral cluster, which reflects the strong electron-lattice coupling in the cluster. The vibrational properties for Se_8 are also presented.

Keywords: First-principles; MD; LAPW; selenium cluster; vibrational properties

1 INTRODUCTION

The structural relaxation associated with the change of the electronic states for selenium compounds and other chalcogenides has received much attention. In accordance with the external conditions and material preparation, the selenium exhibits many allotropes [1, 2]. Especially in the amorphous phase (a-Se), it is known experimentally that there exist a photodarkening phenomena, observed as a red-shift of the optical absorption edge of the light exposed a-Se [3, 4]. As a plausible interpretation of this phenomena, changing of the electronic states originated from the structural change of the constituent atoms is believed to be most relevant. Wong and coworkers [5] have studied the electronic states of the two different structural alignment of selenium chains by a tight-binding calculations. They have reported that the bandgap becomes changed when the alignment changes from one to the another, and that the amount of

change of the bandgap is comparable with the experimental result for the a-Se film [4]. Their calculation assumed the static structures for the selenium clusters. To investigate more details about this phenomena, *ab-initio* calculation with the structural relaxation is most appropriate.

The experimental study for the a-Se by Nagels *et al.* [4] indicates that the prepared a-Se film contains predominantly Se_8-ring like molecular fragments. From this point of view, it is very interesting to investigate the structural, vibrational and electronical properties of Se_8 cluster by the first-principles molecular dynamics (LAPW-MD) simulation based on the LAPW method [6, 7]. As a simplified model of the photoactivated partition for a-Se, we study here the structural properties of the ionized cluster Se_8^+ as well as its electronic state.

In this paper, we will study the equilibrium structure and vibrational properties of the neutral cluster through the LAPW-MD simulation, which are compared with the experiments and other first-principles calculations. For the ionized cluster, changes of the structural and electronical properties from that for the neutral cluster are discussed.

2 CALCULATION

In a previous paper [8], we have presented the details of the first-principles molecular dynamics calculation based on the LAPW method. The present LAPW-MD scheme uses the wave function extrapolation scheme [9] and preconditioned steepest descent (PSD) method [10] generalized to non-orthogonal basis sets.

The PSD equation we have used is

$$\dot{\mathbf{C}}'_i = -\mathbf{K}' \cdot (\mathbf{H}' - \varepsilon_i) \cdot \mathbf{C}'_i \tag{1}$$

where $\mathbf{C}'_i$, $\mathbf{K}'$ and $\mathbf{H}'$ are vector notation of the transformed i'th wave function coefficient, preconditioning operator and Hamiltonian matrix, respectively. Equation (1) has the same form as in the case of the orthogonal basis set, since the applied transformation puts the overlap matrix out of sight. Corresponding applied transformations are [8, 11]:

$$\mathbf{C}'_i \equiv \mathbf{U}\mathbf{C}_i, \quad \mathbf{K}' \equiv \mathbf{U}\mathbf{K}\mathbf{U}^{-1}, \quad \mathbf{H}' \equiv \mathbf{U}^{\dagger -1}\mathbf{H}\mathbf{U}^{-1}. \tag{2}$$

Here $\mathbf{U}$ is the upper half triangle matrix which is determined by Choleski decomposition [12] of the overlap matrix.

For the calculation of Se_8 and Se_8^+, we have used the local-spin-density approximation (LSDA) [13, 14] and a supercell geometry. The von Barth-Hedin's exchange-correlation potential [15] and face-centered-cubic supercell with a dimension of 30 a.u. was used. The cut-off energy of the LAPW basis set was taken as 4 a.u., which corresponds to about 2500 LAPW's. Only a Γ point of the Brillouin zone was taken into consideration as k-point sampling, since we used a sufficiently large supercell. For the calculation in muffin-tin (MT) spheres, we have used 201 points radial mesh with a logarithmic step size of 0.044 a.u. The radius of the MT-sphere was chosen to be $R = 2.0$ a.u. Through our MD simulations, it has been checked that touching of the MT-spheres has never occurred. The spherical harmonics expansion was truncated at $l_{max} = 8$, which was used to expand the wave function, charge density and potentials. Core states are treated fully-relativistically without spin-orbit interactions. The expression for atomic forces in the LAPW method derived by Yu *et al.* [16] has been used. The constant temperature MD simulation with the time step of 50 a.u. has been carried out, in which the temperature control was achieved by a simple velocity scaling method.

3 RESULTS

First we have carried out LAPW-MD calculation for Se_8 cluster to obtain the most stable structure. Initial geometry of a planer ring with small distortion was adopted. In order to search for the stable structure, the artificial damping force proportional to the atomic velocity was added into the original equation of motion, *i.e.*,

$$M_I \frac{d^2 \mathbf{R}_I}{dt^2} = \mathbf{F}_I - \eta M_I \frac{d \mathbf{R}_I}{dt} \tag{3}$$

where the M_I, $\mathbf{R}_I$ and η are the atomic mass, atomic position and damping coefficient, respectively.

The geometrical parameters of the stable structure of Se_8 obtained are summarized in Table I. Our results show a good agreement with the experiment [17] and other first-principles calculation [18] in bond length l, bond angle α, and dihedral angle γ. The experimental data in Table I are those for the crystalline α-monoclinic selenium (α-Se_8), so that the amount of small deviation (within 3%) from our results is considered to be reasonable.

TABLE I The bond length l, bond angle α and dihedral angle γ of the stable structure of Se_8 cluster

	l [a.u.]	α [deg.]	γ [deg.]
Present work	4.37	108	99
Experiment[a]	4.41	106	101
Other calc.[b]	4.42	109	98

[a] Reference [17]
[b] Reference [18]

Second we have carried out a constant temperature (NTV) MD simulation to investigate the vibrational properties of the Se_8 cluster. The stable structure obtained above was chosen to the initial configuration. Temperature was set at 300 K and the MD simulation was carried out for 1.34 ps. Vibrational analyses were calculated by fitting the MD trajectories into the trajectories of a harmonic system as described in Ref. [19]. We have resolved MD trajectories into D_{4d} irreducible representation and determine the vibrational frequencies, amplitudes, eigenvectors. The vibrational spectrum of Se_8 cluster we have obtained is shown in Figure 1 and vibrational frequencies are tabulated in Table II. Both the experimental data [20] and calculated value [21] in this table are for α-Se_8, and the calculated values are the results of the modified Urey-Bradley's force field model. The deviation of the present calculation from the experiment and calculation becomes larger for both higher frequencies and lower frequencies regions. For the former, the deviation is due to the smaller value of the bond length, whereas for the latter, the deviation presumably originates from shortage of the simulation time. Only the low frequency vibrational mode $\nu_8(E_2)$ has not been assigned by the present analysis, which needs much longer time MD simulation.

For the ionized cluster Se_8^+, a uniform background charge was introduced to maintain charge neutrality. The stable structure for the neutral cluster obtained as above was chosen as its initial configuration for Se_8^+ calculation. In the first 100 MD steps, we have used a microcanonical system with the initial temperature $T = 250$ K. During this period, the equilibrium temperature reached to 500 K. The following 1000 MD steps, we have used a constant temperature canonical system at 300 K. After this NTV simulation, the temperature was reduced slowly and finally we have obtained the stable structure of Se_8^+ cluster. The stable structures and geometrical parameters of Se_8 and Se_8^+ are shown in Figure 2. To our knowledge, there is no experimental data about the

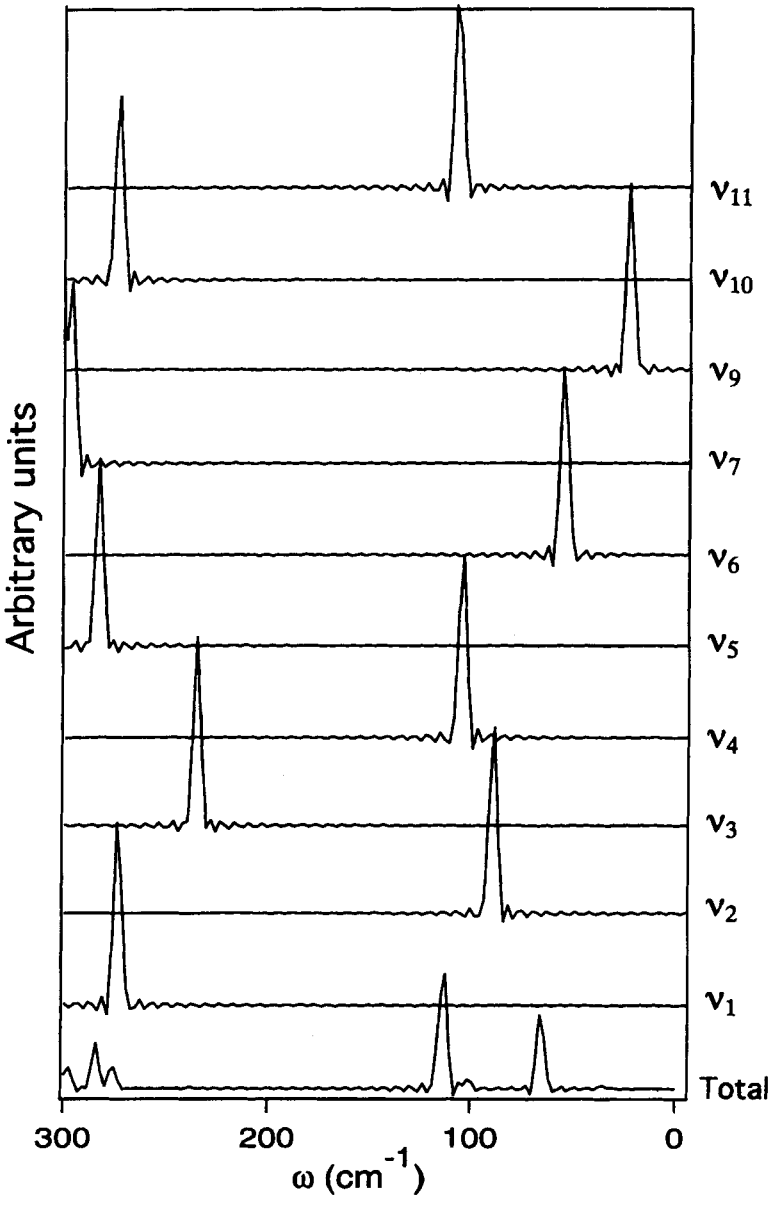


FIGURE 1 Vibrational spectrum of Se_8 obtained by LAPW-MD simulation.

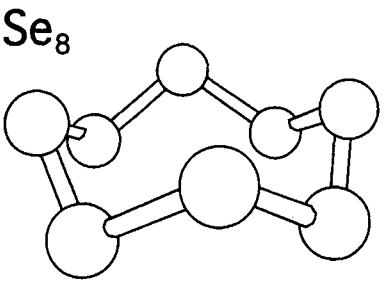
TABLE II Vibrational frequencies (in cm^{-1}) of Se_8 cluster

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}
Symmetry	A_1	A_1	B_1	B_2	E_1	E_1	E_2	E_2	E_2	E_3	E_3
Present work	275	102	238	113	284	65	298	–	35	276	115
Experiment[a]	249	114	216	119	254	95	254	84	50	239	128
Calculated[b]	257	115	224	130	253	111	252	78	44	235	115

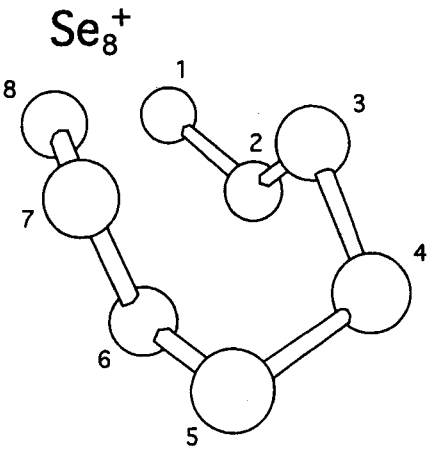
[a] Reference [20]
[b] Reference [21]

stable structure of Se_8^+. From this figure, a large structural change is observed and stable structure of Se_8^+ has a lower symmetry (C_s symmetry) than that of the neutral cluster (D_{4d} symmetry). It turns out that there are three groups of the bond length for Se_8^+: the shortest one corresponds to that for the dimer, the midst one corresponds to that of the neutral cluster Se_8, and the longest bond. It turns out that a nearly parallel aligned structure can be seen in Figure 2 from the fact that the dihedral angles γ_{23} and γ_{67} are nearly the same. Such a parallel alignment structure yields an energetically higher value for the neutral system, because the coulomb repulsion between lone-pair orbitals becomes larger. However, for the ionized cluster, such a structure becomes stable.

Figure 3 shows the Khon-Sham eigenvalue distribution for Se_8 and Se_8^+ at their most stable structure. The origin of the horizontal axis was chosen for halfway between HOMO and LUMO states. For the ionized cluster, the width of the valence band becomes spread compared with the neutral one, and both the HOMO and LUMO states are shifted towards the midgap. From simple analysis of the charge density profile, we have found that the singly occupied HOMO state of Se_8^+ exhibits highly localized and lone-pair like charge density near the atom 1 and 8 in Figure 2. By taking into account the structural and electronical information, it is natural to consider these midgap states as charged defect states [22]. On applying visible light of about 2 eV into a-Se such a remarkable changes of the structural and electronical properties can be promoted, so that many bond reformations will be produced and parallel aligned bonds mentioned above may be possible to form intrinsic bonding defects like one discussed by Wong *et al.* [5] which has shed light on the origin of the photodarkening phenomena.



$l = 4.37$
$\alpha = 108$
$\gamma = 99$



$l_{12} = l_{34} = l_{56} = l_{78} = 4.20$
$l_{23} = l_{45} = l_{67} = 4.38$
$l_{18} = 4.48$

$\alpha_1 = 104$
$\alpha_2 = 103$
$\alpha_3 = 93$
$\alpha_4 = \alpha_5 = 102$
$\alpha_6 = 90$
$\alpha_7 = 108$
$\alpha_8 = 106$

$\gamma_{12} = 61$
$\gamma_{23} = 160$
$\gamma_{34} = 88$
$\gamma_{45} = 52$
$\gamma_{56} = 83$
$\gamma_{67} = 158$
$\gamma_{78} = 61$
$\gamma_{81} = 31$

FIGURE 2 Equilibrium structures and geometrical parameters for Se_8 and Se_8^+. The definition of α and γ is the same as in Ref. [18].

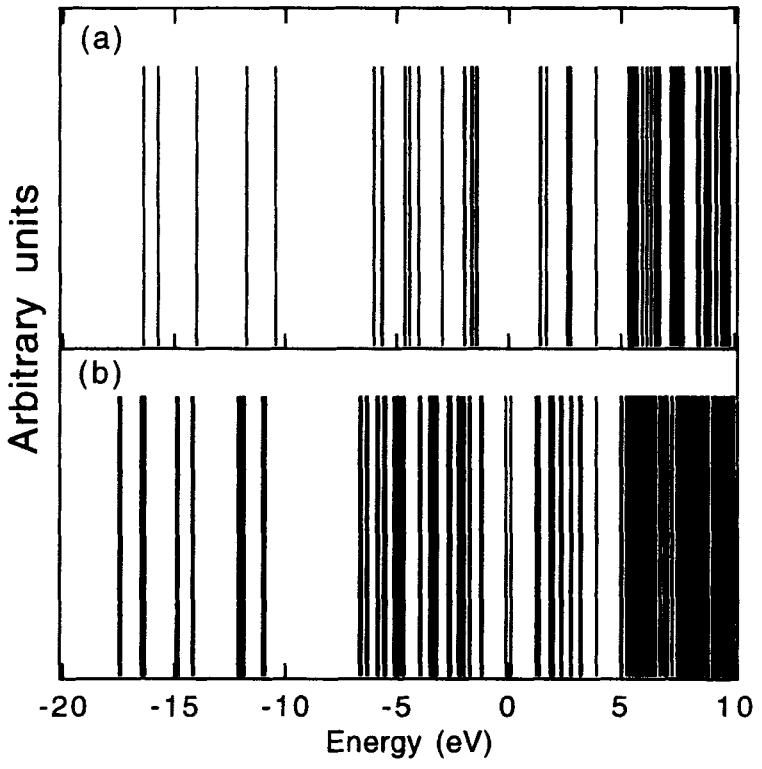


FIGURE 3 Khon-Sham one electron eigenvalue distribution for (a) Se_8 and (b) Se_8^+.

4 CONCLUSIONS

We have investigated the structural and vibrational properties of Se_8 and Se_8^+ clusters via the first-principles LAPW-MD simulations. For the Se_8 cluster, the results obtained are in good agreement with the experiments and other calculations. A remarkable change of the structure for the ionized cluster Se_8^+ from the neutral cluster has been observed. The most stable structure for Se_8^+ obtained presents a characteristic form with the three different bond length and two nearly parallel alignment in the cluster configuration. For the monocations Se_n^+, to our knowledge there is no experimental data about stable structures. Therefore, it would be useful to determine the structures of monocations from experiments, especially for Se_8^+ in the discussion of photodarkening phenomena.

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