Ab initio quasiparticle energy calculations of Ge clusters using the *GW* approximation

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First principles all-electron *GW* calculations are carried out for Ge_n ($n=3-6$) clusters. Although the eigenvalues obtained within the local density approximation of the density functional theory are far off the experiment data, the absolute values of *GW* quasiparticle energy of the highest occupied molecular orbital and the lowest unoccupied molecular orbital are in good agreement with the experimental ionization potentials and electron affinities. For Ge_5 and Ge_6, the change of atomic geometry between the neutral and anion clusters plays a significant role in reproducing the experimental electron affinity. We also show that relativistic effect is not very important for germanium clusters.

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I. INTRODUCTION

Physical properties of clusters are very different from those of crystals. For example, the bulk has a specific value of the energy gap, while clusters have the energy gap strongly depending on the cluster size. Semiconductor clusters such as silicon and germanium clusters have attracted great attention due to their potential in novel optical devices using the size-controlled optical gap. So far, a lot of theoretical as well as experimental studies have been devoted to silicon[1–3] and germanium[4] clusters.

Most of these theoretical studies are based on the density functional theory (DFT), calculating mainly the ionization potential (IP) and the electron affinity (EA) to compare with experimental data. Since the eigenvalues obtained within the local density approximation (LDA) or the generalized gradient approximation do not give the quasiparticle energies, the DFT requires independent calculations of neutral and charged clusters to determine IP and EA. Moreover, this method does not present information on the excitation spectra and excited states. On the other hand, the quasiparticle approach based on the many-body perturbation theory has a merit to give the whole spectra at once in a single calculation. In particular, the first principles *GW* calculation is known to present reliable quasiparticle energy spectra.[5,6]

In our previous paper on silicon clusters,[2] which we will refer to as paper I, we clarified by means of the first principles all-electron *GW* calculation, that the photoemission and inverse photoemission processes are greatly affected by the change of the structures in the ionization process. In particular, Si_n ($n=5,6$) undergo large structural change in the ionization process, resulting in the significant difference between the photoemission and inverse photoemission energies. This is, however, not the common feature of the other clusters, e.g., alkali-metal clusters,[7,8] where this effect is not important because of the large screening among electrons. Therefore, it is interesting to investigate whether germanium clusters behave as silicon clusters.

In the present paper, we extend our previous study paper I and investigate the quasiparticle energy spectra including IPs and EAs for small germanium clusters (Ge_n, $n=3-6$) by means of the first principles all-electron *GW* calculation on the basis of the many-body perturbation theory. We compare our results with the available experimental IPs and EAs to discuss the structural change between neutral clusters and anions. In particular, we will demonstrate the common characteristics in the behavior of silicon and germanium clusters. However, because germanium is heavier than silicon and has $3d$ electrons in the core, we evaluate the semirelativistic terms, i.e., the Darwin and mass-velocity terms in the present calculation.

Our *GW* calculation is based on an all-electron mixed-basis approach in which the one-particle wave function is expanded in linear combination of both atomic orbitals (AOs) and plane waves (PWs). The merit of this approach is that one can treat both the core electron states and the empty free-electron-like states accurately. This GWA all-electron mixed-basis approach has been successfully applied to alkali-metal clusters[7,8] as well as silicon clusters[2] in paper I.

II. METHOD

To calculate the quasiparticle energies, we have to determine the most stable structure of germanium clusters. We performed structural optimization using GAUSSIAN03 package program[9] with B3LYP and confirmed the structures previously determined in Ref. 4. Then, we also performed structural optimization of anion clusters for later use. Figure 1 shows the obtained structures: Ge_3 has the isosceles triangle with C_{2v} symmetry; the two sides are about 2.3 Å. Ge_4 has a rhombus structure with D_{2h} symmetry; each side is 2.5 Å. Ge_5 has a trigonal bipyramid structure with D_{3h} symmetry. Ge_6 has an edge-capped-trigonal bipyramid with C_{2v} symmetry. To compare the total-energy differences with the quasiparticle energies, we evaluated the total energy within the Slater-Vosko-Wilk-Nussair with 6-311+G^* basis set.

Then we employ the GWA all-electron mixed-basis approach to calculate quasiparticle energies. In the calculation, we use an fcc supercell with a cubic edge of 40 a.u., which is carefully chosen to achieve a good convergence of absolute energy levels within the LDA. We also introduce a spherically truncated Coulomb potential, explained in Ref. 10, to avoid interactions between the cells. We use Herman-Skillman[11] code on a radial logarithmic mesh to generate AOs from $1s$ to $4p$. The tails of the $3d$, $4s$, and

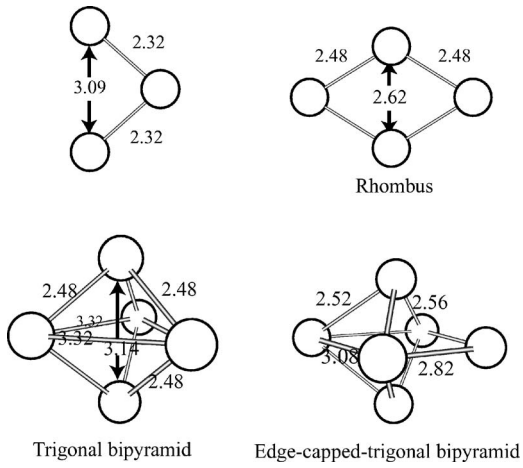

FIG. 1. The geometry of germanium clusters in Ref. 4. The numbers indicate the bond lengths in units of Å.

$4p$ AOs are smoothly truncated within the nonoverlapping atomic spheres. As a result, AOs mainly describe localized part and PWs mainly describe extended part of the states in a unit cell. The cutoff energy for the PWs is taken to be 3.5 Ry for the calculation of LDA wave functions.

In the GWA, the one-electron self-energy operator $\Sigma(\mathbf{r},\mathbf{r}';\omega)$ is defined by (apart from the Hartree potential)

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int e^{i\omega'\eta}G(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r},\mathbf{r}';\omega')d\omega', \tag{1}$$

where G and W denote, respectively, the one-particle Green's function and the dynamically screened Coulomb interaction and η is a positive infinitesimal number. The Fock-exchange part of the self-energy operator Σ_x is obtained by replacing W with the bare Coulomb interaction in Eq. (1), while we call $\Sigma_c=\Sigma-\Sigma_x$ the correlation part. In the present study, we use LDA wave functions and eigenvalues to evaluate G and W from the viewpoint of the perturbation theory. The GWA quasiparticle energy (GWQPE) is then given by

$$E_n^{\mathrm{GWA}} = E_n^{\mathrm{LDA}} + \frac{1}{1-[\partial\Sigma(\omega)/\partial\omega]_{E_n^{\mathrm{LDA}}}}\langle n|\Sigma(E_n^{\mathrm{LDA}}) - \mu_{\mathrm{xc}}^{\mathrm{LDA}}|n\rangle, \tag{2}$$

where E_n^{LDA} and $\mu_{\mathrm{xc}}^{\mathrm{LDA}}$ are the LDA eigenvalue and the exchange-correlation potential, respectively.

In the evaluation of Σ_c, we adopt the generalized plasmon-pole (GPP) model and use 2000 empty levels, corresponding to about 25 eV in the calculations. The cutoff energy for the $\mathbf{G}$, $\mathbf{G}'$ vectors in Fourier space is taken to be 1.2 Ry for the calculation of Σ_c. The GPP model reproduces the experimental quasiparticle energies well.[2,6,8] As far as the handling of the valence levels is concerned, we did not include $3d$ electrons in the calculation of the GPP model. The result did not change very much when we included or excluded $3d$ electrons. The core contribution is also ignored in Σ_c. On the other hand, for the evaluation of Σ_x in Fourier space, we use the cutoff energy of 31.8 Ry to fully take into account the core contribution (see Table I for the evaluated Σ_x values which are typically $-6--17$ eV). We carefully checked that all contributions are well converged with these cutoff energies and the number of empty levels within the accuracy of 0.1 eV. Other technical details of the present calculations are explained in Refs. 7 and 8.

TABLE I. The comparison (in eV) of the GWQPEs (E_n^{GWA}) for the HOMO and LUMO levels of germanium clusters with the LDA eigenvalues (E_n^{LDA}), the LDA total-energy differences (ΔE) and the experimental ionization potentials (Ref. 12) and electron affinities (Ref. 13) with minus signs (E_n^{expt}). The final result E_n^{GWA} is evaluated through Eq. (2): $\mu_{\mathrm{xc},n}^{\mathrm{LDA}}=\langle n|\mu_{\mathrm{xc}}^{\mathrm{LDA}}|n\rangle$, $\Sigma_{x,n}=\langle n|\Sigma_x|n\rangle$, and $\Sigma_{c,n}=\langle n|\Sigma_c|n\rangle$ are the expectation values of, respectively, the LDA exchange-correlation potential, and the exchange and correlation parts of the self-energy Σ. In the first column, Ge_n and $\mathrm{Ge}_n^{(-)0}$ denote neutral clusters with the geometry optimized under neutral and negatively charged conditions, respectively. E_n^{GWA} of $\mathrm{Ge}_n^{(-)0}$ $(n=5,6)$ is corrected by the total-energy difference $\delta E=E(\mathrm{Ge}_n^{(-)0})-E(\mathrm{Ge}_n)$ of neutral systems. (Refs. 2 and 14).

		E_n^{LDA}	ΔE	$\mu_{\mathrm{xc},n}^{\mathrm{LDA}}$	$\Sigma_{\mathrm{x},n}$	$\Sigma_{\mathrm{c},n}$	E_n^{GWA}	E_n^{expt}
Ge_3	HOMO	−5.69	−8.62	−11.78	−14.10	−0.11	−7.93	−7.97∼−8.09[a]
	LUMO	−4.49	−2.69	−10.36	−6.85	−0.92	−2.11	−2.23±0.01[b]
Ge_4	HOMO	−5.61	−8.20	−12.20	−14.67	−0.14	−7.75	−7.87∼−7.97[a]
	LUMO	−4.40	−2.51	−9.87	−6.65	−1.16	−2.07	−1.94±0.05[b]
Ge_5	HOMO	−5.90	−8.52	−11.21	−12.95	−0.40	−7.88	−7.87∼−7.97[a]
	LUMO	−3.83	−2.76	−11.45	−8.22	−0.68	−1.48	
$\mathrm{Ge}_5^{(-)0}$	LUMO	−5.30	−2.76	−11.24	−8.40	−0.12	−2.34	−2.51±0.05[b]
Ge_6	HOMO	−5.74		−12.12	−14.39	0.10	−7.72	−7.58∼−7.76[a]
	LUMO	−3.81	−2.48	−11.39	−8.14	−0.86	−1.61	
$\mathrm{Ge}_6^{(-)0}$	LUMO	−4.95	−2.48	−11.55	−8.27	−0.86	−2.24	−2.06±0.05[b]

[a]Reference 12.
[b]Reference 13.

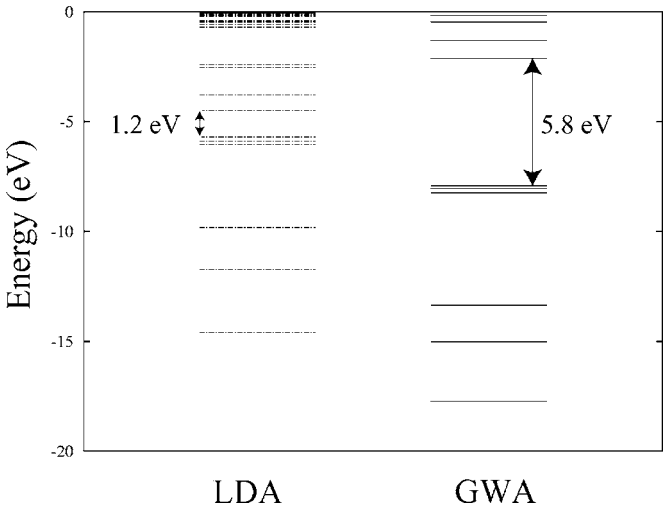

FIG. 2. The energy levels of Ge_3 obtained from the present *GW* calculation (solid lines), compared with the LDA eigenvalues (broken lines). These energy levels include the highest and lowest levels. Experimental HOMO-LUMO gap of Ge_3 is 5.8 eV (Refs. 12 and 13).

III. RESULTS AND DISCUSSION

In Fig. 2, we show energy levels of Ge_3 including the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels obtained from the present LDA and GWA calculations. Although the LDA HOMO-LUMO gap is smaller than the experimental value by about 4.6 eV, the HOMO-LUMO gap obtained from the *GW* calculation agrees well with the experimental HOMO-LUMO gap.

In Table I, the *GW* quasiparticle energies (GWQPEs), E_n^{GWA} are listed in the table compared to the LDA energy eigenvalues E_n^{LDA}, the LDA total-energy differences ΔE, and the experimental IPs (Ref. 12) and EAs (Ref. 13) with minus signs E_n^{expt}. In the same table, we also show the contributions to the GWQPEs, i.e., the expectation values of, respectively, the LDA exchange-correlation potential $\mu_{\mathrm{xc}}^{\mathrm{LDA}}$, and the exchange part Σ_x and the correlation part Σ_c of the self-energy. In the first column, Ge_n $(n=3-6)$ denotes neutral clusters with the most stable ground-state geometry, while $Ge_5^{(-)0}$ and $Ge_6^{(-)0}$ denote neutral clusters with the optimized geometry of anions. The total-energy difference equals to $\Delta E=E(Ge_n^{(-)-})-E(Ge_n)$, where Ge_n and $Ge_n^{(-)-}$ denotes the neutral ground state of the optimized geometry of a neutral cluster and the negatively charged ground state of the optimized geometry of an anion, respectively. For the hexamer, the total energy was not able to be converged by GAUSSIAN03, so the total-energy difference column is left blank. Here the GWQPEs for the LUMO level of Ge_5 and Ge_6 were determined by the structure of anion clusters and corrected by the total energy difference between two neutral systems with this structure and with neutral structure (see the discussion below). For the LUMO level of Ge_3 and Ge_4 and the HOMO level of Ge_n $(n=3-6)$, we calculated the GWQPEs by using neutral structure, because the structural change between neutral and charged clusters is small.

TABLE II. The results of the semi-relativistic correction and the GWQPEs (in eV) for the HOMO and LUMO levels of germanium clusters together with the experimental ionization potentials (Ref. 12), electron affinities (Ref. 13) with minus signs (E_n^{expt}). The results of GWQPEs include the correction of relativistic effect. In the first column, Ge_n and $Ge_n^{(-)0}$ denote neutral clusters with the geometry optimized under neutral and negatively charged conditions, respectively. E_n^{GWA} of $Ge_n^{(-)0}$ $(n=5,6)$ is corrected by the total-energy difference $\delta E=E(Ge_n^{(-)0})-E(Ge_n)$ of neutral systems (Refs. 2 and 14).

		correction	E_n^{GWA}	E_n^{expt}
Ge_3	HOMO	0.05	−7.88	−7.97 ~ −8.09[a]
	LUMO	0.05	−2.08	−2.23±0.01[b]
Ge_4	HOMO	0.02	−7.73	−7.87 ~ −7.97[a]
	LUMO	0.08	−1.99	−1.94±0.05[b]
Ge_5	HOMO	0.05	−7.83	−7.87 ~ −7.97[a]
	LUMO	0.08	−1.40	
$Ge_5^{(-)0}$	LUMO	0.09	−2.25	−2.51±0.05[b]
Ge_6	HOMO	0.03	−7.69	−7.58 ~ −7.76[a]
	LUMO	0.07	−1.54	
$Ge_6^{(-)0}$	LUMO	0.11	−2.13	−2.06±0.05[b]

[a]Reference 12.
[b]Reference 13.

In Table II, we show the semirelativistic correction for the HOMO and LUMO levels of germanium clusters together with the experimental data. In the third column, the correction denotes the GWQPE difference between calculations including relativistic effect and excluding relativistic effect. The correction is 0.02–0.11 eV, and the final results are not changed much. In the case of bulk germanium, it is well known that, in the LDA level calculation, the semirelativistic effect dramatically reduces the value of the energy gap even to negative, i.e., the germanium crystal becomes gapless, and only the GWA with the semirelativistic effect reproduces very well the experimental energy gap.[6] However, for germanium clusters, we find from this table that the semirelativistic corrections to IP and EA are 0.02–0.11 eV (all positive and small) for Ge_n $(n=3-6)$ and their HOMO-LUMO gap is not affected by this correction.

In Figs. 3–5, we show the cluster-size dependences of the HOMO-LUMO gap, the HOMO energy, and the LUMO energy obtained in the present *GW* calculation, compared with the LDA eigenvalues, the LDA total-energy differences and the experimental data. In Fig. 3, the GWA results agree well with the experimental HOMO-LUMO gap, although the corresponding LDA results always underestimate the experimental values by about 4–5 eV. The cluster size dependence of the HOMO-LUMO gap is small for Ge_n $(n=3-6)$. This behavior is similar to Si_n $(n=4-6)$ reported in paper I. For metallic clusters, for example, the HOMO-LUMO gap almost monotonically decreases as the cluster size increases except for magic number clusters.[7,8] This difference may be related to the fact that planar structures of Ge_3 and Ge_4 (see Fig. 1) make it difficult to construct covalent bonds. Here the GWQPEs for the LUMO level of Ge_5 and Ge_6 were deter-

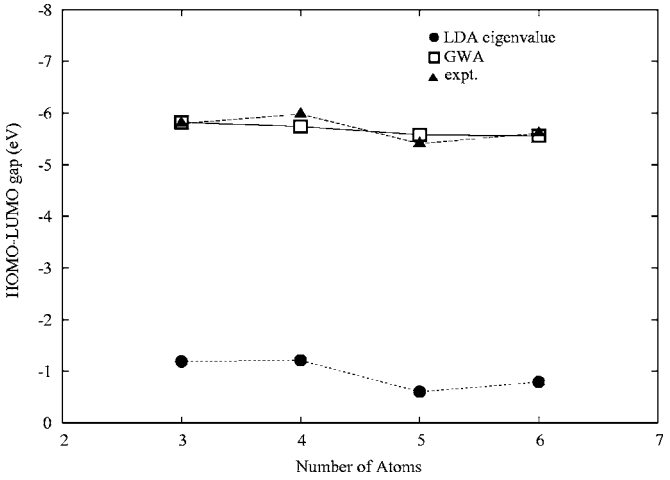

FIG. 3. The cluster-size dependence of the HOMO-LUMO gap (E_g eV) obtained from the present *GW* calculations (□), compared with the LDA eigenvalues (●) and the experimental HOMO-LUMO gaps (▲) calculated from the relation E_g=IP−EA. (□) and (●) of the pentamar and hexamer show the *GW* result and the LDA eigenvalue using the structure of anion cluster.

mined by the structure of anion clusters and corrected by the total energy difference between two neutral systems with this structure and with neutral structure (see the later discussion). For the LUMO level of Ge_3 and Ge_4 and the HOMO level of Ge_n (n=3–6), we calculated the GWQPEs by using neutral structure, because the structural change between neutral and charged clusters is small.

As is seen in Fig. 4, for the HOMO levels of all the clusters studied here, the GWQPEs agree well with the experimental IPs with minus signs (E_n^{expt}), although the corresponding LDA eigenvalues E_n^{LDA} always underestimate the experimental values by about 2 eV. The LDA total-energy differences overestimate the experimental values by about 0.5 eV.

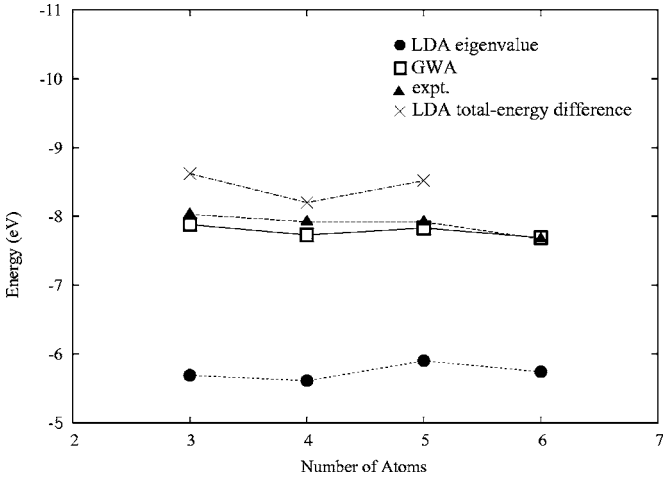

FIG. 4. The cluster-size dependence of HOMO quasiparticle energy (IP with minus sign) obtained from the present *GW* calculations (□), compared with the LDA eigenvalues (●), the LDA total-energy differences (×) and the experimental ionization potentials (▲) (Ref. 12).

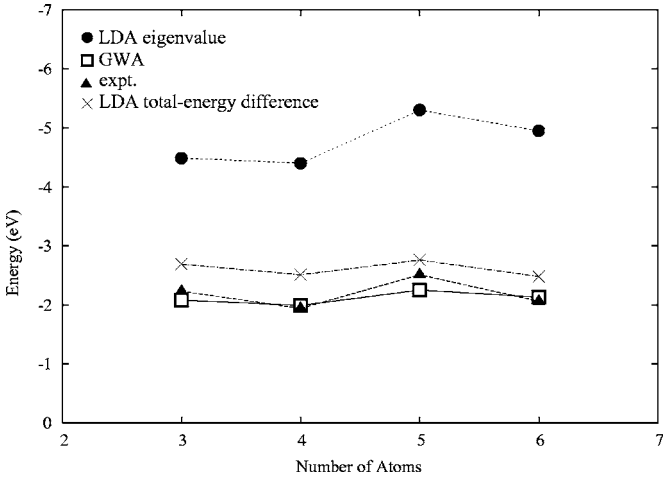

FIG. 5. The cluster-size dependence of LUMO quasiparticle energy (EA with minus sign) obtained from the present *GW* calculations (□), compared with the LDA eigenvalues (●), the LDA total-energy differences (×), and the experimental electron affinities (▲). (□) and (●) of the pentamar and hexamer show the *GW* result and the LDA eigenvalue using the structure of anion cluster (see the text).

For the LUMO levels (Fig. 5), the GWQPEs agree well with the experimental EAs with minus signs, although the corresponding LDA eigenvalues overestimate the experimental EAs by about 2 eV. The LDA total-energy differences overestimate the experimental values by about 0.3–0.5 eV. Here, the GWQPEs using the geometry of $Ge_5^{(-)0}$ and $Ge_6^{(-)0}$ are plotted in Fig. 5. On the contrary, the GWQPEs using the geometry of Ge_5 and Ge_6 underestimate the experimental EA by about 1 and 0.4 eV, respectively. The quasiparticle energies are greatly improved, reflecting that the structures are largely different between Ge_n and Ge_n^- (n=5,6). As is shown in Fig. 6, the structural change between the neutral cluster and anion is so large in Ge_n (n=5,6) that one cannot ignore this difference. In the *horizontal* direction, bond length differences between (a1) (Ge_5^-) and (b1) (Ge_5) and between (a2) (Ge_6^-) and (b2) (Ge_6) are about 0.3 Å. In the *vertical* direc-

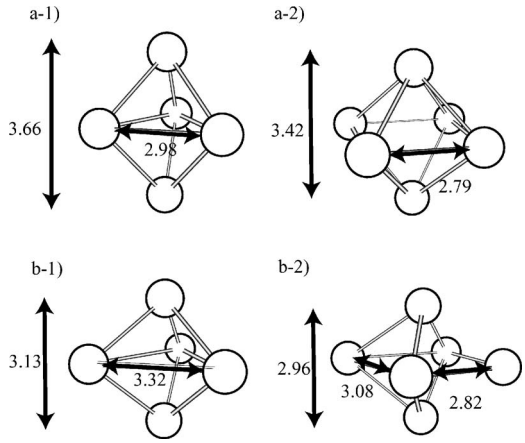

FIG. 6. The geometry of (a) negatively charged germanium clusters Ge_5^- and Ge_6^- and (b) neutral germanium clusters Ge_5 and Ge_6 in Ref. 4. The numbers indicate the bond lengths in units of Å.

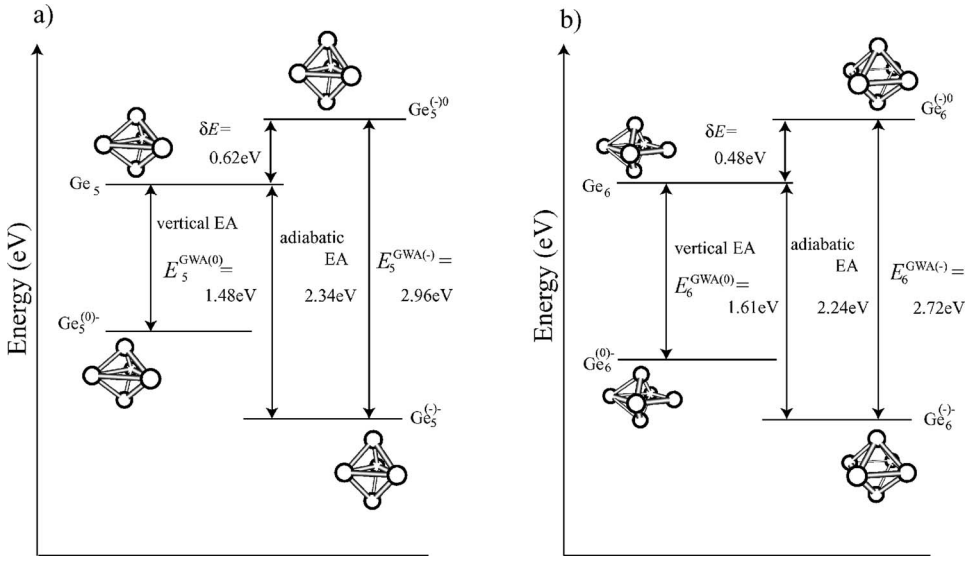

FIG. 7. Total-energy difference between the anion and neutral clusters for (a) Ge_5 and (b) Ge_6, estimated by using the different geometries optimized with neutral or negatively charged condition. These values are calculated within the LSA.

tion, bond length differences between (a1) and (b1) and between (a2) and (b2) are about 0.5 Å. The structural change between anion and neutral clusters in pentamer accompanies change of the bond length more than 10% in each direction. In the case of hexamer, even the symmetry of the structure changes from C_{2v} to D_{4h}. The agreement with the experiments for the trimer and tetramer can be attributed to the fact that the structures are similar between Ge_n and Ge_n^- for $n=3$ and 4.

Let us consider the EA in more detail. In experimental EA measurements, first the system is negatively charged and then the energy to remove an electron is measured. The threshold of the first peak in the photoelectron spectrum is interpreted as the adiabatic EA. Adiabatic EA measurement involves a structural change. In Fig. 7, we show the total-energy diagram for (a) pentamer and (b) hexamer, employing different geometries with charged and neutral conditions. $E_n^{\mathrm{GWA}(0)}$ and $E_n^{\mathrm{GWA}(-)}$ $(n=5,6)$ correspond, respectively, to the GWQPEs calculated using the neutral and anion clusters. The values of $\delta E=E(\mathrm{Ge}_n^{(-)0})-E(\mathrm{Ge}_n)$ shown in the diagram are evaluated within the LDA. The EA in the present *GW* calculation is the energy gain in the vertical process when neutral cluster is charged up with one extra electron $E_n^{\mathrm{GWA}(0)}=E(\mathrm{Ge}_n^{(0)-})-E(\mathrm{Ge}_n)$. When we calculate the EA using the optimized geometry of Ge_n, the obtained value presents this EA. On the other hand, the adiabatic EA measurements correspond to the total-energy difference between $\mathrm{Ge}_n^{(-)-}$ and Ge_n. Therefore, if we determine the optimized geometry of anions $(\mathrm{Ge}_n^{(-)0})$, the adiabatic EAs correspond to the LUMO quasiparticle energies of $\mathrm{Ge}_n^{(-)0}$ [i.e., $E_n^{\mathrm{GWA}(-)}=E(\mathrm{Ge}_n^{(-)-})-E(\mathrm{Ge}_n^{(-)0})$ in Fig. 7], corrected by the total-energy difference $\delta E=E(\mathrm{Ge}_n^{(-)0})-E(\mathrm{Ge}_n)$ between two neutral systems, $\mathrm{Ge}_n^{(-)0}$ and Ge_n. In Fig. 7, the difference between the vertical EAs $(E_n^{\mathrm{GWA}(0)})$ and the adiabatic EAs is 0.86 and 0.63 eV, respectively, for $n=5$ and 6. Therefore, it is essential to calculate quasiparticle energies employing the structures of anion clusters to compare with the experimental EAs. In the GWA, the vertical EAs are calculated at once, while the adiabatic EAs are calculated in a way described here. As a result, the good agreement is achieved between the present results $(\mathrm{Ge}_n^{(-)0}, n=5,6$, LUMO) and the experimental adiabatic EAs.

Thus, in the present study, we found that the structural change of germanium clusters is very important as well as silicon clusters reported in paper I. In both germanium and silicon clusters, the pentamer and hexamer undergo large structural change in the photoemission process, and the resulting EAs are significantly affected by this change. Here, we notice that the geometries of Ge_n and Si_n have the same symmetry for each $n=3-5$ and have slightly different symmetries (C_{2v} and D_{4h}) for $n=6$. More importantly, both for Ge_n and Si_n, the trimer and tetramer have planar structures, while the pentamer and hexamer have three-dimensional structures. Their electronic structures are also similar for each n (for example, the character of the electronic states is the same between Ge_n and Si_n except for $n=6$ for which the symmetry is different but similar). That the structural change is significant for three-dimensional structures $(n=5,6)$ may be attributed to the covalent bonds showing strong angle dependence. According to the population of an additional electron, such structures can be largely deformed by ionization. The volumes of Ge_5, Ge_5^-, Ge_6, and Ge_6^- are 4.98, 4.69, 8.56, and 8.81 $Å^3$ respectively. That is, the pentamer shrinks by about 6% when one extra electron is added to the neutral one, while the anion of hexamer is expanded by 3%. This behavior corresponds to the fact that the EA of Ge_5 is larger than that of Ge_6.

IV. CONCLUSION

In summary, the first principles all-electron *GW* calculation was carried out for small germanium clusters. The resulting GWQPEs for the HOMO levels are in good agree-

ment with the experimental IPs for all clusters studied here, while the GWQPEs for the LUMO levels are in agreement with the experimental EAs. If the systems are negatively charged, the structural changes affect the GWQPEs very much, in particular, for the LUMO levels of Ge_5 and Ge_6. In this paper as well as the previous paper I concerning silicon clusters (Ref. 2), we have manifested that there is a phenomenon similar to a strong Stokes shift between the photoemission process and its inverse process. In fact, the vertical EAs are significantly different between these two processes. On the other hand, the effect of ion relaxations becomes important in the adiabatic EAs. The corresponding GWA results are in good agreement with the experimental EAs (Ref. 13), when the necessary energetic correction is taken into account. We also showed that the relativistic effect is not very important for germanium clusters Ge_n $(n=3-6)$ in contrast to bulk germanium.

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[1] C. Zhao and K. Balasubramanian, J. Chem. Phys. **116**, 3690 (2002).
[2] S. Ishii, K. Ohno, V. Kumar, and Y. Kawazoe, Phys. Rev. B **68**, 195412 (2003).
[3] C. Xu, T. R. Taylor, G. R. Burton, and M. Neumark, J. Chem. Phys. **108**, 1395 (1998).
[4] E. F. Archibong and A. St-Amant, J. Chem. Phys. **109**, 962 (1998); C. Zhao and K. Balasubramanian, *ibid.* **115**, 3121 (2001), and references therein.
[5] L. Hedin, Phys. Rev. **139**, A796 (1965).
[6] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985).
[7] S. Ishii, K. Ohno, Y. Kawazoe, and S. G. Louie, Phys. Rev. B **63**, 155104 (2001).
[8] S. Ishii, K. Ohno, Y. Kawazoe, and S. G. Louie, Phys. Rev. B **65**, 245109 (2002).
[9] GAUSSIAN 03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
[10] G. Onida, L. Reining, R. W. Godby, R. DelSole, and W. Andreoni, Phys. Rev. Lett. **75**, 818 (1995).
[11] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).
[12] S. Yoshida and K. Fuke, J. Chem. Phys. **111**, 3880 (1999).
[13] G. R. Burton, C. Xu, C. C. Arnold, and D. M. Neumark, J. Chem. Phys. **104**, 2757 (1996).
[14] The results of E_n^{GWA} for $Ge_n^{(-)0}$ were determined from the GWQPEs calculated for the geometry of anions, corrected by the total-energy difference $\delta E = E(Ge_n^{(-)0}) - E(Ge_n)$ between two neutral systems $Ge_n^{(-)0}$ and Ge_n.