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Formation of stable fullerenelike Ga_nAs_n clusters ($6 \leq n \leq 9$): Gradient-corrected density-functional theory and a genetic global optimization approach

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Based on gradient-corrected density-functional theory and genetic global optimization approach that directly searches for the configuration of greatest stability, we are able to find particularly stable structures for binary gallium arsenide clusters. We report a formation of fullerenelike Ga_nAs_n clusters with $6 \leq n \leq 9$ due to the enhanced ionic characteristics of the Ga-As bonding. The IR and optical spectra of the Ga_nAs_n clusters are calculated, which are useful and important to distinguish the isomer structures and to examine the predicted trend of structural transitions by experiments.

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I. INTRODUCTION

Gallium arsenide play a significant role in the semiconductor microelectronics.[1] The understanding of the structures, bonding, and physical properties of GaAs clusters is important for the growth mechanism of GaAs-based materials[1] and for the application of low-dimensional GaAs nanostructures.[2] Experimental studies on GaAs clusters include mass spectra,[4] photodissociation,[5] ultraviolet photoelectron spectra (UPS),[6] chemical reactivity,[7] polarizabilities,[8] and photoabsorption spectra.[9]

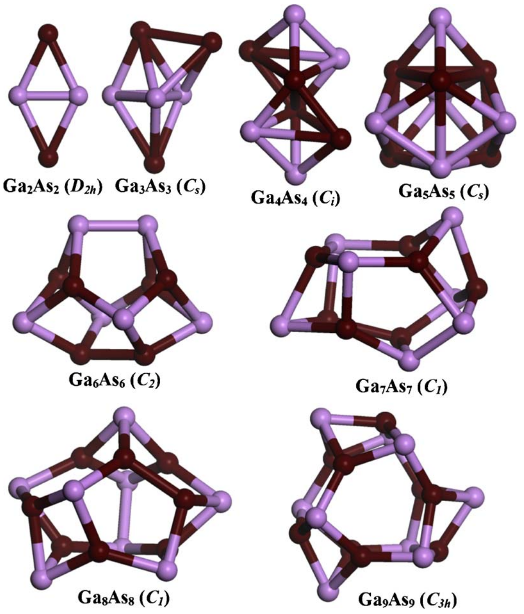
For GaAs surface, the reconstruction from bulk *sp* hybridization[3] leads to an unoccupied dangling bond on Ga atoms as well as lone-pair electrons on As atoms. This results in the removal of the dangling bond states from the gap region in the surface density of state, making the GaAs surface semiconducting.[10] The measurement of ammonia chemisorption on Ga_nAs_n clusters[7] ($n=3-8$) suggested that GaAs clusters adopt alternating Ga-As bonding arrangement characteristics resembling GaAs crystal surfaces. The measured photodetachment thresholds also indicate that all Ga_nAs_n clusters ($n \geq 2$) have singlet closed-shell electronic configurations with a substantial energy gap Δ between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).[6] The photoabsorption spectra[9] of GaAs clusters have shown that the transition from molecularlike to bulklike behavior occurs at Ga_7As_7, and that the Ga_nAs_n clusters with $n \geq 7$ behave like small bulklike nanocrystallites.

On the theoretical side, the lowest-energy structures of Ga_nAs_n with $n \leq 5$ have been extensively studied and well understood.[11–15] However, less work has been done on Ga_nAs_n clusters with $n \geq 6$. The small Ga_nAs_n clusters ($n \leq 5$) have similar structures to the isoelectronic Ge_{2n} clusters, in which both Ga-As and Ga-Ga/As-As bonds can be found. Thus, it would be important to elucidate the size-dependent structural evolution from small Ge_{2n}-like structure towards bulklike surfaces and nanocrystallites with alternating Ga-As bonding. In this paper, we address this issue by performing an unbiased search for the lowest-energy structures of Ga_nAs_n up to $n=9$. We found a family of GaAs cluster structures. The enhanced ionic characteristics of the Ga-As bonding for $n=9$ gives high-symmetry fullerenelike GaAs clusters. The optical properties of GaAs clusters were discussed, which link our theoretical predictions with experimental measurements.

II. COMPUTATIONAL METHODS

To conduct an unbiased search of the ground state structure of Ga_nAs_n, we generated a number of isomers (typically between 30 and 60) for each cluster size using a genetic algorithm[16] (GA) with a Stillinger-Weber potential fitted for GaAs solid.[17] All-electron density functional theory (DFT) calculations using a DMOL program[18] were then performed to determine the lowest-energy structures of GaAs clusters and to compute their electronic properties. A double numerical basis set that includes *d*-polarization functions[18] (DND) was used. In the DFT calculations, the density functional was treated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation potential.[21] Vibrational frequency calculation and normal mode analyses have been performed on the lowest-energy structures to simulate the infrared (IR) spectra and to confirm that they are true minima on the photoemission spectroscopy (PES).

The optical properties of the Ga_nAs_n clusters were further studied using time-dependent density-functional theory (TD-DFT) formalism of Casida[19,20] implemented in the Gaussian 03 program. In TD-DFT, the time-dependent analog of the exchange-correlation functional is a functional of the time-dependent electron density. Since the exact time-dependent exchange-correlation functional is not known, a reliable adiabatic local density approximation is employed and standard time-independent exchange-correlation func-



Ga_2As_2 (D_{2h}) Ga_3As_3 (C_s) Ga_4As_4 (C_i) Ga_5As_5 (C_s)

Ga_6As_6 (C_2) Ga_7As_7 (C_1)

Ga_8As_8 (C_1) Ga_9As_9 (C_{3h})

FIG. 1. (Color online) Lowest-energy structures of Ga_nAs_n clusters (n=2–9).

tional derived for ground-state DFT, i.e., PBE functional, is used for practical calculations.

In the GA search, the structures generated by Stillinger-Weber potentials provide a variety of candidates structures for representing different regions in the potential energy surface, which can be further examined within DFT-PBE level. Indeed, in our global search using the combined technique, we have even included some high-energy isomers on the Stillinger-Weber potential energy surface. The global geometry optimization of atomic cluster containing more that 10 atoms ($n>5$ for a Ga_nAs_n compound cluster), as a well-known nondeterministic polynomial (NP)-hard problem, is a big challenge to computational physics and cluster physics. Although our method is not guaranteed to locate the true global minima on the entire potential energy surface, it is among the most efficient and robust methods available nowadays. The structural trend revealed in our global search should not sensitively rely on the details of the computational results. The efficiency and validity of the combined scheme of empirical GA search and DFT optimization were demonstrated in our previous works on other atomic clusters.[16]

III. RESULTS AND DISCUSSIONS

A. Lowest-energy structures of Ga_nAs_n clusters

The lowest-energy structures obtained for Ga_nAs_n (n=2–9) clusters are shown in Fig. 1. Our main theoretical results are summarized in Table I. We successfully reproduced the previously predicted ground state structures for Ga_nAs_n clusters with n=2–5.[11–14] Our lowest-energy structure for Ga_6As_6 is energetically preferred over that in Ref. 15 by 0.35 eV. The detailed discussion of the structural isomers of each size and the comparison to the previous results will be given in a forthcoming paper. The current theoretical scheme was validated in the GaAs diatomic molecule and GaAs solid in zinc-blende structure. For the ground state GaAs molecule with triplet multiplicity, the theoretical bond length (2.597 Å), binding energy (2.20 eV), ionization potential (7.32 eV), and vibrational frequency ($187.4\ cm^{-1}$) from our DFT-PBE calculations using DMOL program compare well with experimental data (2.53 ±0.02 Å, 2.06±0.05 eV, 7.17±0.75 eV, $215\ cm^{-1}$).[22] For GaAs solid, the DFT-PBE calculations predict equilibrium Ga-As bond length d=2.494 Å and cohesive energy E_c=3.37 eV/atom, in agreement with experimental values of d=2.448 Å, E_c=3.26 eV/atom.[23]

As reported in previous calculations,[11–15] small Ga_nAs_n clusters have similar structures with its isolelectronic Ge_{2n} clusters.[24] For example, Ga_2As_2 and Ga_5As_5 have rhombus and tetracapped trigonal prism structures, similar to Ge_4 and Ge_{10}, respectively. Starting from n=6, a cage-based structural growth pattern mainly with Ga-As alternating arrangement was found for Ga_nAs_n. Ga_6As_6 has a basketlike structure consisting of sixteen Ga-As bonds, one Ga-Ga bond, and one As-As bond. More spherical Ga-As alternating cages were obtained for larger Ga_nAs_n clusters with n

TABLE I. Binding energies (E_b, eV/atom), HOMO-LUMO gap (Δ, eV), optical gap (E_g, eV), vertical ionization potential (E_{vip}, eV), polarizibility per atom (α, $Å^3$/atom), and average on-site charge (Q, e) on Ga or As atoms of the ground states of Ga_nAs_n (n=2–9) clusters. The numbers in parentheses are experimental data.

n	Structure (symmetry)	E_b	E_{vip}	Δ	E_g	α	Q
2	Rhombus (D_{2h})	2.257	7.359	1.289	2.490	8.813	0.173
3	Capped trigonal bipyramid (C_s)	2.537	7.220	2.077	2.370	3.430(4.0±0.8)	0.179
4	Rhombic prism (C_i)	2.591	6.989	1.435	2.057	4.217(4.2±0.8)	0.211
5	Tetracapped trigonal prism (C_i)	2.715	7.353	1.766	1.980	4.334(4.7±0.4)	0.252
6	Basketlike (C_2)	2.748	7.020	1.208	1.260	4.073(3.9±0.3)	0.375
7	Cage (C_1)	2.819	6.913	1.331	1.665	3.656(4.3±1.6)	0.410
8	Cage (C_1)	2.840	6.817	1.053	1.099	3.663(4.5±0.4)	0.461
9	BN fullerenelike cage (C_{3h})	2.879	6.928	0.977	1.564	3.741(4.8±0.3)	0.526
∞	Zinc-blende structure	3.370	4.483	0.630			0.471

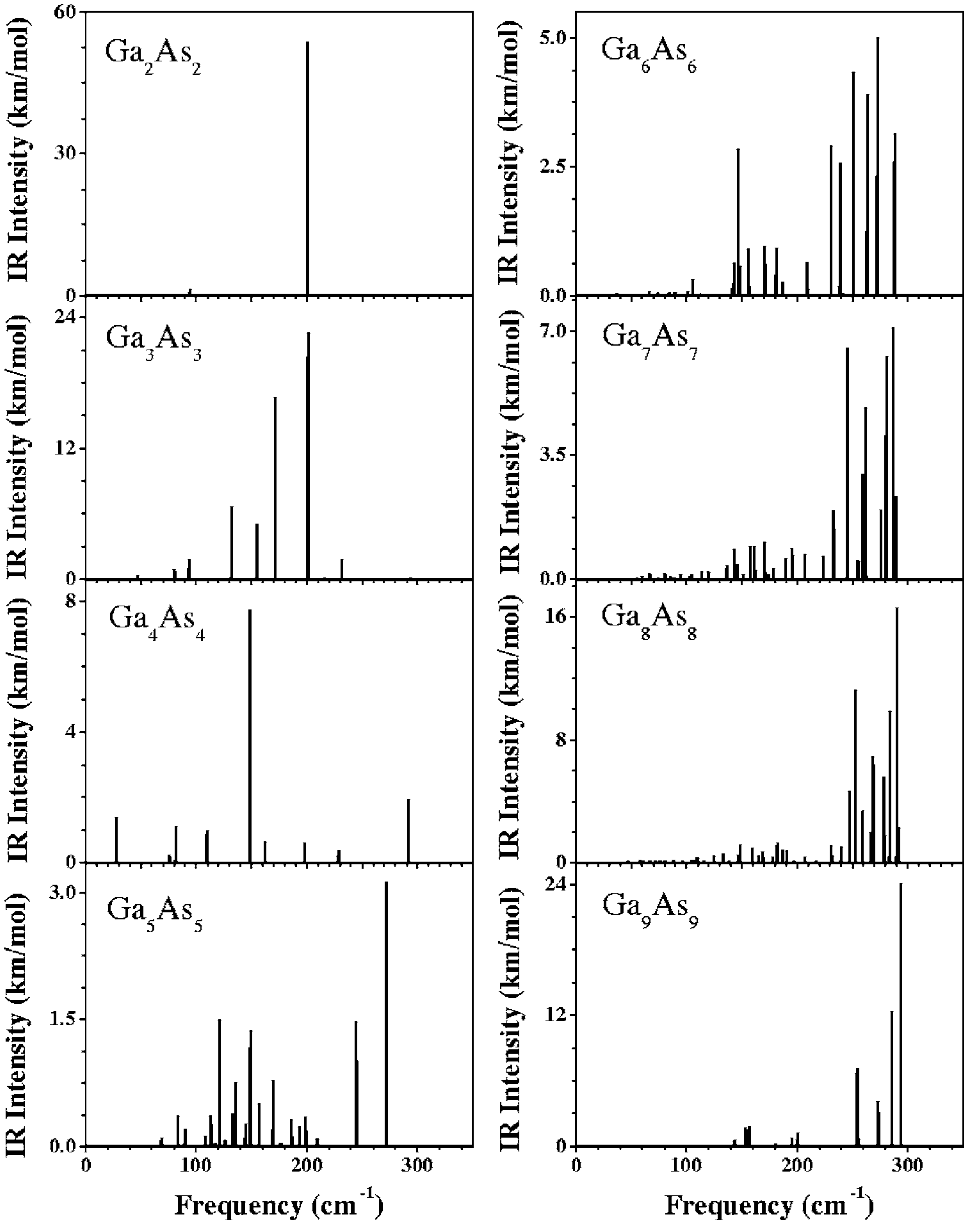


FIG. 2. Simulated IR spectra for Ga_nAs_n clusters ($n=2-9$).

$=7-9$. There are only one Ga-Ga and one As-As bond in both Ga_7As_7 and Ga_8As_8 cages. A completely alternating arrangement of Ga and As atoms was observed for Ga_9As_9 cage. It should be noted that similar B-N alternating cages were previously found for small BN clusters.[25] As clusters become larger, hollow cage configurations would become less stable and the stuffed fullerene cages precursor of nanocrystalline structure are expected, as observed in the medium-sized Si (Ref. 26) and CdSe (Ref. 27) nanoclusters. The global geometry optimization of larger Ga_nAs_n clusters with $n \geq 10$ is still in progress.

To understand the present finding of cage structures with Ga-As alternations, we study the characteristics of chemical bonding in GaAs clusters. Since the electronegativity (EN $=2.0$) of As is slightly larger than that ($\mathrm{EN}=1.6$) of Ga, the Ga-As bond is partially polarized. Thus, although the Ga-As bonding is still primarily covalent, the polarity in the Ga-As bonding will result in atomic structures that are different from Ge clusters. As shown in Table I, there is a substantial increase of charge transfer between Ga and As atoms as cluster size increases. For smaller clusters with $n=2-5$, the average on-site charge Q is between $0.17e$ and $0.25e$, which are 36% to 53% of the bulk value ($Q=0.471e$). As a consequence, the bonding of clusters would be mainly covalent so that the smaller Ga_nAs_n clusters behave like Ge_{2n} clusters. Both Ga_6As_6 and Ga_7As_7 are in the transition region with an average on-site charge $Q \approx 0.4e$, 85% of the bulk value. In the larger Ga_8As_8 and Ga_9As_9, their on-site charges are comparable to the bulk value. The emergence of GaAs alternating cage structures, which become energetically favored only at $n > 5$, leads to enhanced ionic bonding character. Since the electronegativity difference between As and Ga is relatively small (only 0.4 difference), the GaAs clusters show less ionic bonding characteristics than the BN clusters ($\mathrm{EN}=2.0$ for B and $\mathrm{EN}=3.0$ for N). Thus, unlike the BN clusters in which the ion with the same sign charge adjacent to one another is quite energetically unfavorable, Ga-Ga and As-As bonds can still be found in the lowest-energy structures of GaAs clusters.

This family of GaAs clusters shows remarkable size-dependent physical properties. As shown in Table I, the binding energy per atom from Ga_2As_2 to Ga_9As_9 increases monotonically from 67% to 85% of the bulk value. This implies that the cohesion of Ga_nAs_n clusters with up to $n=9$ is already rather close to the bulk GaAs solid. As the cluster size increases, the computed ionization potential generally decreases towards the bulk limit. But the vertical ionization potential of Ga_9As_9 is still much higher than the work function of bulk GaAs solid (4.483 eV from our calculation, 4.07 from experiment). Except for Ga_2As_2, the polarizabilities of Ga_nAs_n ($n=3-9$) are all around 4.0 Å^3/atom, in agreement with experiments.[8]

B. IR and optical absorption of Ga_nAs_n clusters

To characterize the atomic structures and chemical bonding, we compute the vibrational frequencies and IR spectra of Ga_nAs_n ($n=2-9$) clusters using the DMOL program. The results are presented in Fig. 2. For smaller Ga_nAs_n with $n \leq 5$, most peaks of IR spectra are located below 200 cm^{-1}. For larger clusters with $n=7-9$, the dominant IR peaks are blueshifted to the higher-frequency region of about 250–300 cm^{-1}. The blueshift of IR frequencies with increasing cluster size corresponds to the transition from covalent to partial ionic bonding in GaAs clusters as well as the enhanced strength of chemical bonding during the transition (it should be noted that the gradual transition with clusters with $n=5,6,7$ being intermediate does correlate with structures: the clusters at $n=8,9$ are perfectly alternating, and structures for $n=5,6,7$ are "partially alternating" although it is almost perfectly alternating for $n=6,7$). For comparison, the computed vibrational frequencies for the zone-center optical phonons (Γ point in the q space) of GaAs solid in zinc-blende structure are 76.9 cm^{-1}, 212.5 cm^{-1}, 232.8 cm^{-1}, 245.2 cm^{-1}, and 261.5 cm^{-1}, respectively. The predicted trend in IR spectra of Ga_nAs_n clusters could be validated in future experiments.

To further characterize the physical properties of the clusters, we study the optical excitations and absorption spectra of Ga_nAs_n ($n=2-9$) clusters. The results are presented in Fig. 3. It is found that the absorption spectra of Ga_nAs_n clusters predicted by TD-DFT calculations display significant blueshifts with respect to the time-independent Kohn-Sham eigenvalue spectra. The difference between TD-DFT and time-independent Kohn-Sham spectra becomes more profound as the cluster size increases. In Fig. 3, the absorption spectra of two different isomers of Ga_8As_8 are included, which clearly demonstrate that the spectra are sensitive to geometry. Namely, our calculations show a substantial variety of the spectral shapes and peak positions for different GaAs clusters. Thus, gallium arsenide clusters can be identified by their absorption spectra in gas-phase experiments. Even for gallium arsenide clusters with the same size and chemical composition, their optical absorption spectra are quite sensitive to the atomic geometry and this effect can be used to distinguish isomers.[14] Similar observations for the spectra of silicon and other clusters have been reported earlier[28] and recently.[19,20] Moreover, we find that the optical absorption spectra of Ga_nAs_n clusters exhibit long absorption tails, which extend deeply into the region of lower transition energies. Such behavior is absent in the optical absorption of semiconductor quantum dots[14] and cannot be described in terms of a simple quantum confinement theory. Quantum dots are truncated fragments of the bulk structure which are passivated at the boundaries.[14] Unlike clusters considered in this work, they do not possess free surfaces.[14] On this basis, we believe that the low-energy absorption can be attributed to the existence of reconstructed free surfaces in the clusters. Our results are consistent with the calculations of Vasiliev *et al.*[14] As far as the symmetry is concerned, the absorption tail for $n=9$ is not pronounced as that for $n=6,7,8$ since Ga_9As_9 has a higher symmetry than Ga_nAs_n ($n=6,7,8$) (see Table I) and the symmetry plays an important role in determining the optical activity. As shown in Fig. 3, the first singlet excitation for $n=9$ is dipole forbidden, while those for $n=6,7,8$ are dipole allowed. The photoabsorption gap is usually associated with the first allowed transition in the excitation spectrum.[20] Here we note that the intensity of the first allowed excitation is too weak to be detected in experiments.

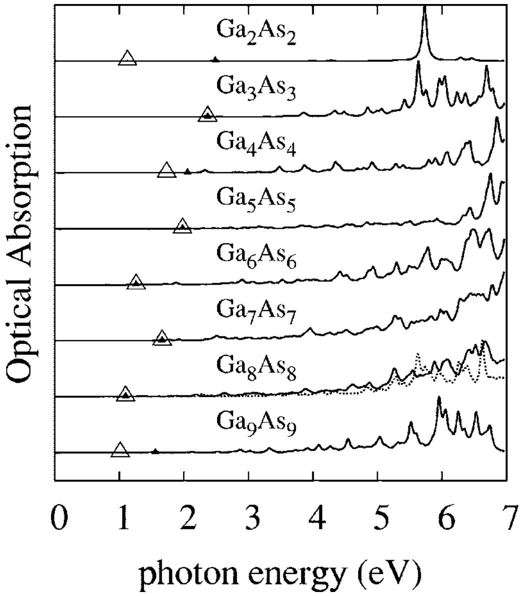


FIG. 3. Optical adsorption spectra (in arbitrary units) of Ga_nAs_n clusters ($n=2-9$) from TD-DFT calculations. A Gaussian convolution of 0.04 eV has been used to simulate a finite broadening of the calculated spectra. The open and filled triangles mark the first singlet excitation and the first dipole-allowed excitation in the excitation spectrum. For Ga_8As_8, we include the spectra for lowest-energy structure (solid line) and a metastable isomer (dashed line).

IV. SUMMARY

In summary, we have employed a combined optimization strategy of global genetic algorithm search and local DFT minimization to determine the lowest-energy structures of Ga_nAs_n clusters up to $n=9$. We have found a family of fullerenelike Ga_nAs_n clusters with $n=6-9$. Our results demonstrate that the chemical bonding in Ga_nAs_n clusters start to behave like bulk GaAs from $n=6-7$. The enhanced ionic bonding characteristics in Ga_nAs_n clusters with $n=9$ results in Ga-As alternating fullerenelike structures. The theoretical IR and optical spectra are useful and important to distinguish the isomer structures and to validate the predicted trend of structural transitions experimentally.

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[1] M. J. Howes and D. V. Morgan, *Gallium Arsenide: Materials, Devices, and Circuits* (Wiley, New York, 1985).

[2] E. Donkor, in *Encyclopedia of Nanoscience and Nanotechnology*, edited by H. S. Nalwa (American Scientific Publishers, Stevenson Ranch, California, 2004), Vol. 3, pp. 703–517.

[3] L. Butler, G. Redmond, and D. Fitzmaurice, J. Phys. Chem. **97**, 10750 (1993).

[4] S. C. O'Brien, Y. Liu, Q. Zhang, J. R. Heath, F. K. Tittel, R. F. Curl, and R. E. Smalley, J. Chem. Phys. **84**, 4074 (1986).

[5] Q. L. Zhang, Y. Liu, R. F. Curl, F. K. Tittel, and R. E. Smalley, J. Chem. Phys. **88**, 1670 (1988).

[6] C. Jin, K. J. Taylor, J. Conceicao, and R. E. Smalley, Chem. Phys. Lett. **175**, 17 (1990).

[7] L. Wang, L. P. F. Chibante, F. K. Tittel, R. F. Curl, and R. E. Smalley, Chem. Phys. Lett. **172**, 335 (1990).

[8] R. Schäfer, S. Schlecht, J. Woenckhaus, and J. A. Becker, Phys. Rev. Lett. **76**, 471 (1996).

[9] R. Schäfer and J. A. Becker, Phys. Rev. B **54**, 10296 (1996).

[10] X. Zhu, S. B. Zhang, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **63**, 2112 (1989), and references therein.

[11] L. Lou, L. Wang, L. P. F. Chibante, R. T. Laaksonen, P. Nordlander, and R. E. Smalley, J. Chem. Phys. **94**, 8015 (1991).

[12] W. Andreoni, Phys. Rev. B **45**, 4203 (1991).

[13] K. M. Song, A. K. Ray, and P. K. Khowash, J. Phys. B **27**, 1637 (1994).

[14] I. Vasiliev, S. Ogut, and J. R. Chelikowsky, Phys. Rev. B **60**, R8477 (1999).

[15] J. Y. Yi, Chem. Phys. Lett. **325**, 269 (2000).

[16] J. J. Zhao and R. H. Xie, J. Comput. Theor. Nanosci. **1**, 117 (2004).

[17] Z. Q. Wang and D. Stroud, Phys. Rev. B **42**, 5353 (1990).

[18] B. Delley, J. Chem. Phys. **92**, 508 (1990).

[19] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[20] R. H. Xie, G. W. Bryant, G. Sun, T. Kar, Z. Chen, V. H. Smith, Jr., Y. Araki, N. Tagmatarchis, H. Shinohara, and O. Ito, Phys. Rev. B **69**, 201403(R) (2004); R. H. Xie, G. W. Bryant, C. F. Cheung, V. H. Smith, Jr., and J. J. Zhao, J. Chem. Phys. **121**, 2849 (2004); R. H. Xie, G. W. Bryant, J. J. Zhao, T. Kar, and V. H. Smith, Jr., Phys. Rev. B **71**, 125422 (2005); J. R. H. Xie, C. F. Cheung, and J. J. Zhao, J. Comput. Theor. Nanosci. **3**, 312 (2006).

[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[22] G. W. Lemire, G. A. Bishea, S. A. Heidecke, and M. D. Morse, J. Chem. Phys. **92**, 121 (1990).

[23] G. S. Rohrer, *Structure and Bonding in Crystalline Materials* (Cambridge University Press, Cambridge, England, 2001).

[24] J. J. Zhao, J. L. Wang, and G. H. Wang, Phys. Lett. A **275**, 281 (2000); J. L. Wang, G. H. Wang, and J. J. Zhao, Phys. Rev. B **64**, 205411 (2001).

[25] D. L. Strout, J. Phys. Chem. A **105**, 261 (2001).

[26] S. Yoo, J. J. Zhao, J. L. Wang, and X. C. Zeng, J. Am. Chem. Soc. **126**, 13845 (2004); J. L. Wang, X. L. Zhou, G. H. Wang, and J. J. Zhao, Phys. Rev. B **71**, 113412 (2005); J. J. Zhao, J. L. Wang, J. Jellinek, S. Yoo, and X. C. Zeng, Eur. Phys. J. D **34**, 35 (2005).

[27] A. Kasuya, R. Sivamohan, Y. A. Barnakov, I. M. Dmitruk, T. Nirasawa, V. R. Romanyuk, V. Kumar, S. V. Mamykin, K. Tohji, B. Jeyadevan, K. Shinoda, T. Kudo, O. Terasaki, Z. Liu, R. V. Belosludov, V. Sundararajan, and Y. Kawazoe, Nat. Mater. **3**, 99 (2004).

[28] S. Ogut, J. R. Chelikowsky, and S. G. Louie, Phys. Rev. Lett. **79**, 1770 (1997); I. Vasiliev, S. Ogut, and J. R. Chelikowsky, *ibid.* **82**, 1919 (1999); **86**, 1813 (2001); I. Vasiliev, J. R. Chelikowsky, and R. M. Martin, Phys. Rev. B **65**, 121302(R) (2002).