

## Structure and stability of cluster-assembled solid $\text{Al}_{12}\text{C}(\text{Si})$ : A first-principles study

X. G. Gong\*

*National Laboratory of Solid State Microstructures, Institute for Solid State Physics, Nanjing University,  
Nanjing 210093, People's Republic of China*

*and Centro Brasileiro de Pesquisas Físicas, Rua Dr. Xavier Sigaud, 150-Urca, Rio de Janeiro, Brazil*

(Received 19 September 1996; revised manuscript received 18 December 1996)

We have proposed a possible crystal structure for the cluster-assembled solid  $\text{Al}_{12}\text{C}(\text{Si})$ , and its electronic structures and stability have been studied in the framework of density functional theory and *ab initio* molecular dynamics. We find that  $\text{Al}_{12}\text{C}(\text{Si})$  clusters are condensed by van der Waals force, with a very small cohesive energy of  $\sim 1.1$  eV. The combined steepest descent on ions shows that upon the formation of solid the relaxation of atomic distances in the  $\text{Al}_{12}\text{C}(\text{Si})$  cluster is very small. The stability of the  $\text{Al}_{12}\text{C}$  solid is also confirmed by a dynamical simulation at low temperature. [S0163-1829(97)02427-2]

In the past decades, a great deal of effort has been devoted to the synthesizing and the fundamental understanding of new materials in an atomic dimension.<sup>1</sup> With the discovery of the  $\text{C}_{60}$  molecule and its solid phase,<sup>2</sup> an enormous interest in the study of cluster and cluster-assembled materials has been aroused. Since the properties of clusters are quite different from that of atoms, it is reasonable to expect that the cluster-assembled materials have unusual properties, which would be quite different from that in the atomic solid phase, like what was observed in solid  $\text{C}_{60}$ .<sup>3</sup> Generally to synthesize a cluster-assembled solid, stable cluster, as the building block of the solid, is necessary, and also the interaction between the clusters should be much smaller than the interaction in the cluster. Otherwise when the clusters are brought together, the structure of cluster would coalesce to form another phase. Moreover, since the cluster is not completely spherical-like, the geometric effects can play a crucial role on the formation of the cluster-assembled solid.

Recently, from the total energy and electronic structure calculations,<sup>4</sup> it had been found that the stability of  $\text{Al}_{13}$  cluster can be significantly enhanced by doping with a tetravalent carbon atom. Since there exists about a 2 eV gap between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO), the interaction between the  $\text{Al}_{12}\text{C}(\text{Si})$  cluster can be expected to be small. Therefore the  $\text{Al}_{12}\text{C}(\text{Si})$  cluster is suggested to be a good candidate to form a cluster-assembled solid. In fact, the high stability of  $\text{Al}_{12}\text{C}$  cluster was confirmed by a few recent studies.<sup>5,6</sup> Seitsonen *et al.*<sup>6</sup> studied the dynamical stability of  $\text{Al}_{12}\text{C}$  cluster by the Car-Parrinello method, and they found that, even above 900 K, the structure of  $\text{Al}_{12}\text{C}$  cluster remains icosahedral-like, which indicates that the  $\text{Al}_{12}\text{C}$  cluster is indeed stable. Moreover, Kawai<sup>5</sup> has studied the interaction between two  $\text{Al}_{12}\text{C}$  clusters by the Car-Parrinello method, they found that the structure of  $\text{Al}_{12}\text{C}$  clusters remains unchanged. However no successful studies for the cluster-assembled  $\text{Al}_{12}\text{C}$  solid have been made. Seitsonen *et al.*<sup>6</sup> studied the properties of  $\text{Al}_{12}\text{C}$  solid with the fcc-like structure, but they found that the total energies increased monotonically with the decreasing of the lattice constant, and there is no local minimum which is necessary for the formation of a metastable phase. For the  $\text{Al}_{12}\text{Si}$  solid with fcc-like

structure, a very short Al-Al bond length between clusters<sup>12</sup> is found, its bond energy was even larger than that in the Al bulk. So obviously the fcc-like  $\text{Al}_{12}\text{Si}$  solid would also not be stable, since the structure of icosahedral  $\text{Al}_{12}\text{Si}$  cluster would coalesce.

As discussed by Khannan and Jena, the geometric effects are important in the cluster-assembled materials.<sup>7</sup> In the icosahedral  $\text{Al}_{12}\text{C}(\text{Si})$  cluster, although 12 aluminum atoms are homogeneously distributed on a spherical surface, it cannot be rotational invariant like a rare-gas atom. It is well known that, even in the icosahedral fullerene of  $\text{C}_{60}$ , which has a smoother surface since it contains 60 carbon atoms on the surface, various phases with different rotational order have been observed at low temperature.<sup>8</sup> Obviously, the relative orientation of clusters may play an important role in the formation of a solid from the icosahedral  $\text{Al}_{12}\text{C}(\text{Si})$  clusters.

In this paper, based on the limited search in the configuration space, we propose a crystal structure for the cluster-assembled  $\text{Al}_{12}\text{C}(\text{Si})$  solid. In the total energy calculations, we have obtained an energy minimum and we do find that the interaction between the clusters in  $\text{Al}_{12}\text{C}(\text{Si})$  solid is very weak, and the cohesive energy is very small. By performing the combined steepest descent on the ions and electrons, and the dynamical simulation at low temperature, we show that the  $\text{Al}_{12}\text{C}$  solid is a stable van der Waals solid.

The recent simulations on the cluster dimer (two icosahedral 13-atom clusters) with the Leonard-Jones potential show that,<sup>9</sup> the relative cluster orientation is very important for the stability of the cluster dimer. If we put 12 surface atoms of a body-center icosahedron on the six faces of a cubic box, the most stable structure for a cluster dimer is with two cubic boxes in alternated orientation of  $90^\circ$ , as shown in Fig. 1. In fact, only in this configuration, the mass centers of two icosahedrons can be approached more closely than any other isomers which have higher energies, as confirmed by the charge density shown below. This suggests that, when the clusters are brought together, they should be properly arranged according to their geometric shape. In fact, the intuitive fcc-like structure, which is the lowest energy structure for the atomic van der Waals solid, was proved to be unstable for cluster-assembled  $\text{Al}_{12}\text{C}$  solid and  $\text{Al}_{12}\text{Si}$  solid. So, we have tried to design a structure for  $\text{Al}_{12}\text{C}(\text{Si})$  solid, in

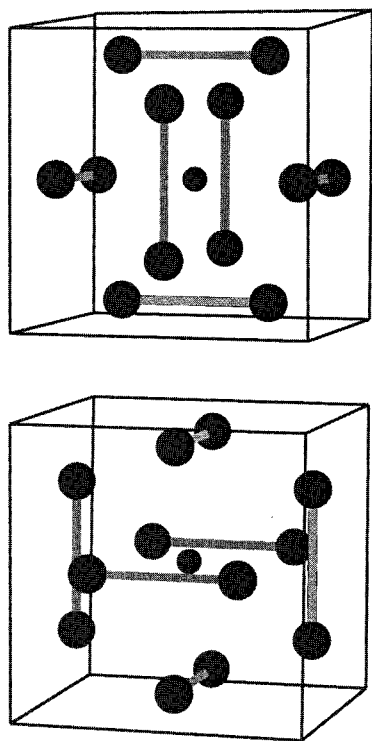


FIG. 1. The atomic structure of  $\text{Al}_{12}\text{C}$  cluster dimer, and the relative orientation of  $\text{Al}_{12}\text{C}$  clusters in solid phase. Big balls for Al atoms and small balls for C atoms.

which each  $\text{Al}_{12}\text{C}(\text{Si})$  cluster is alternated  $90^\circ$  with all its nearest neighbors. This turns out to be a cubiclike crystal structure, each unit cell contains eight  $\text{Al}_{12}\text{C}(\text{Si})$  clusters. Actually, a similar structure has been observed in  $AB_{13}$  system,<sup>10</sup> where  $B_{13}$  has an icosahedral structure, the large atom A is believed to be an electron donor to close the electronic shell of  $B_{13}$  which makes  $B_{13}$  stable.<sup>11</sup> To show whether this structure is stable for  $\text{Al}_{12}\text{C}$  solid, we have performed a first-principles calculation and *ab-initio* molecular-dynamics simulation, and its stability is confirmed. With the same crystal structure, we have studied the properties of the cluster-assembled solid  $\text{Al}_{13}\text{K}$ , which was suggested to have a CsCl structure,<sup>13</sup> but recent calculation showed that an icosahedral  $\text{Al}_{13}\text{K}$  cluster would not be stable in CsCl structure.<sup>14</sup> The results on  $\text{Al}_{13}\text{K}$  will be published elsewhere.

All our calculations are based on the density functional theory with the local density approximation<sup>15</sup> and Car-Parrinello method.<sup>16</sup> The electronic density is expressed in terms of Kohn-Sham orbitals,<sup>17</sup> which are expanded into plane waves with an energy cutoff of 35 Ry for carbon and 14 Ry for silicon. Only the valence electrons are treated explicitly and their interactions with the ionic cores are described by the Bachelet-Hamann-Schluter type pseudopotentials<sup>18</sup> with *sp* nonlocality. The minimization of the energy functional is performed with a conjugate gradient for the fixed atomic distances and is also combined with the steepest descent for electrons and ions in  $\text{Al}_{12}\text{C}$  solid at a lattice constant of 30.8 a.u. We have used a time step of 4.0 a.u. and fictitious mass of 300 a.u. for electrons in all the calculations.

First, we have calculated the equilibrium structure for the isolated  $\text{Al}_{12}\text{C}$  and  $\text{Al}_{12}\text{Si}$  cluster. Since our method is based on the plane wave, it is necessary to use the periodical boundary condition. To erase the interaction between the cluster and its images, one need to use a big unit cell. The test shows that a fcc-like unit cell with a lattice constant of 33 a.u. is enough to make the interaction negligible. By calculating the binding energies at various atomic distances, the obtained equilibrium distances are 4.66 a.u. and 4.89 a.u. for Al-C and Al-Si bonds, respectively, which is the same as the result obtained by Seitsonen *et al.*,<sup>6,12</sup> but it is smaller than the previous results obtained by other *ab initio* methods with a localized basis function.<sup>4</sup> We have obtained binding energies of 45.9 eV and 44.7 eV for an isolated  $\text{Al}_{12}\text{C}$  and  $\text{Al}_{12}\text{Si}$  cluster, respectively, which are very close Seitsonen's results. These results are also in agreement with the results of other previous *ab initio* methods.<sup>19</sup> As we can see from Table I, it seems that the calculations based on atomic orbitals give systematically larger atomic distances compared with the results from pseudopotentials. But the difference of bond lengths between  $\text{Al}_{12}\text{Si}$  cluster and  $\text{Al}_{12}\text{C}$  cluster is consistent with the pseudopotential's results. It is also worth noting that the binding energies of the  $\text{Al}_{12}\text{Si}$  cluster and  $\text{Al}_{12}\text{C}$  cluster are very close in various calculations. Since the atomic size of the silicon atom is larger than the carbon atom, the obtained Al-Si bond length is also larger than the Al-C bond length.

To calculate the cohesive energy of  $\text{Al}_{12}\text{C}(\text{Si})$  solids with the structure presented above, we have used a primitive cell with two  $\text{Al}_{12}\text{C}(\text{Si})$  clusters. The obtained total energies via the lattice constant, relative to the isolated clusters, are

TABLE I. Comparison of the binding energy ( $E_b$ ) and the nearest neighbor distance for icosahedral  $\text{Al}_{12}\text{Si}$  and  $\text{Al}_{12}\text{C}$  clusters.

	$\text{Al}_{12}\text{Si}$		$\text{Al}_{12}\text{C}$	
	$d(\text{Al-Si})$ (a.u.)	$E_b$ (eV)	$d(\text{Al-C})$ (a.u.)	$E_b$ (eV)
Present <sup>a</sup>	4.89	44.7	4.68	45.9
Seitsonen <i>et al.</i> <sup>b</sup>	4.89	44.9	4.69	45.3
Gong and Kumar <sup>c</sup>	5.22	39.2	5.05	40.6
Khanna and Jena <sup>c</sup>	5.05	39.2	4.78	41.1

<sup>a</sup>See, also, Ref. 2.

<sup>b</sup>References 6 and 12.

<sup>c</sup>Reference 4.

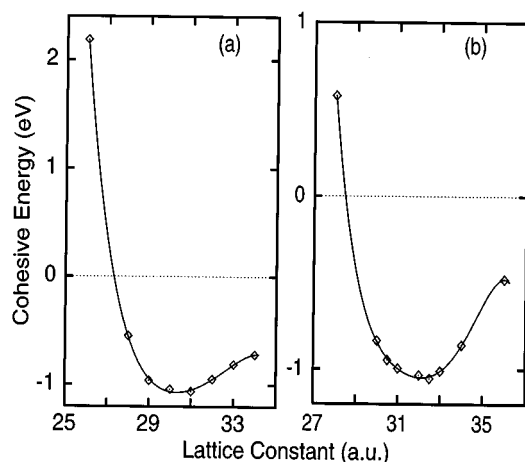


FIG. 2. The cohesive energies for the cluster-assembled  $\text{Al}_{12}\text{C}(\text{Si})$  solids. The solid line is the guide for the eye. The left panel for the  $\text{Al}_{12}\text{C}$  solid and the right panel for the  $\text{Al}_{12}\text{Si}$  solid.

shown in Fig. 2. In contrary to the result of the fcc-like solid, we have obtained an energy minimum at the lattice constant  $\sim 30.8$  a.u. and  $\sim 32.5$  a.u. for the  $\text{Al}_{12}\text{C}$  solid and  $\text{Al}_{12}\text{Si}$  solid, respectively, which indicates that the  $\text{Al}_{12}\text{C}(\text{Si})$  solid could be formed with this lattice constant. The very small cohesive energy of  $\sim 1.1$  eV, which is comparable to  $\sim 1.6$  eV for the  $\text{C}_{60}$  solid,<sup>3</sup> implies that the  $\text{Al}_{12}\text{C}(\text{Si})$  clusters are condensed by a rather weak van der Waals force. Similar to the  $\text{C}_{60}$  solid in which intracluster C-C distance is almost twice the intercluster C-C distance, the shortest Al-Al distance between different clusters in the  $\text{Al}_{12}\text{C}(\text{Si})$  solid is about 9.2 a.u. (9.9 a.u.), which is much longer than the normal Al-Al bond in bulk aluminum, therefore it is very difficult for Al atoms from different clusters to have a stronger interaction than the van der Waals interaction. These features are also visible in the contour map of the valence charge density. Figure 3 shows the charge density of  $\text{Al}_{12}\text{C}$ . In fact, the main feature in the charge density of  $\text{Al}_{12}\text{Si}$  is very simi-

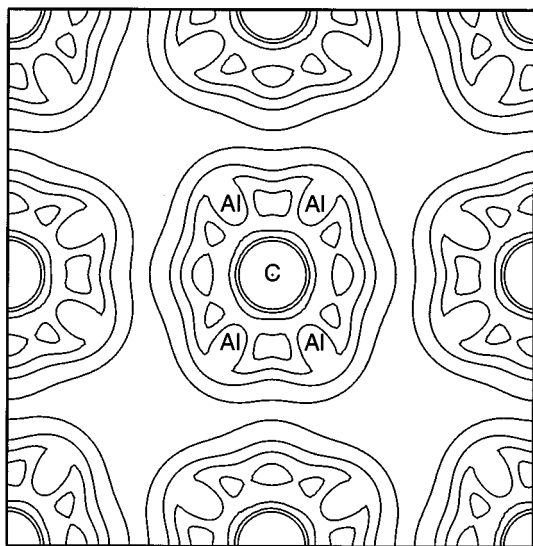


FIG. 3. The contour map of charge density on (001) plane for  $\text{Al}_{12}\text{C}$ .

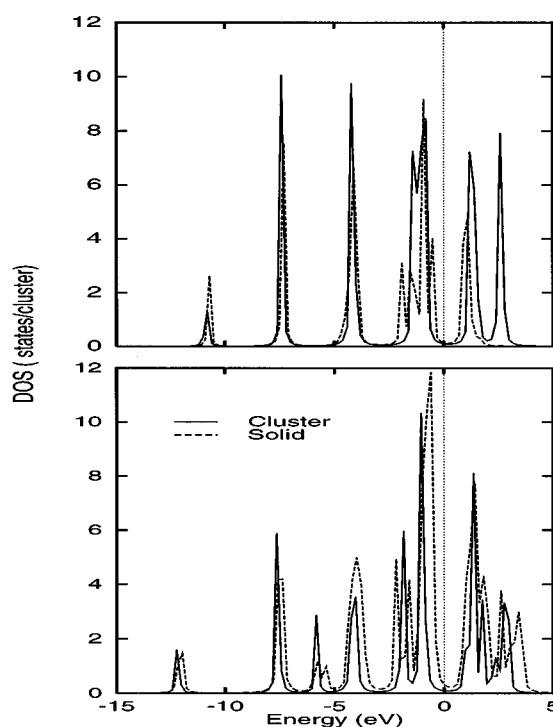


FIG. 4. The electronic density of states for cluster-assembled solids (solid line) and clusters (dash line). The up panel for  $\text{Al}_{12}\text{Si}$  and the lower panel for  $\text{Al}_{12}\text{C}$ .

lar to what observed in  $\text{Al}_{12}\text{C}$ . From Fig. 3 we can see that the charge density of  $\text{Al}_{12}\text{C}$  cluster in solid is almost the same as the charge density of the isolated cluster, and the charge density overlap between the clusters is very small leading to a stable cluster-assembled solid. It is worth noting that the charge density of  $\text{Al}_{12}\text{C}$  cluster (visible from Fig. 3) is not spherical-like. At one axis direction, the charge density has a tendency to move inwards to the center of carbon, and at another axis direction, the charge density has a tendency to move outwards from the center of carbon. So the neighboring clusters need to rotate  $90^\circ$  in order to bring them closer without distorting the charge density significantly. While in fcc-like  $\text{Al}_{12}\text{C}(\text{Si})$  solid, these *inwards* and *outwards* features in charge density cannot be well matched. This may be one of the reasons why the fcc-like  $\text{Al}_{12}\text{C}(\text{Si})$  solid is not stable.

At the equilibrium lattice constants, which corresponds to the energy minimum in Fig. 2, we have calculated the total energies by changing the atomic distances in the clusters. We find that changes for Al-C(Si) bonds are very small. Then when we have performed the combined steepest descent on ions and electrons, a very small relaxation on the structure has been observed again with the energy gaining only about 0.02 eV. These results clearly indicate that the icosahedral structure of the isolated  $\text{Al}_{12}\text{C}(\text{Si})$  cluster remains unchanged upon forming a solid, and it is stable against the steepest descent.

The electronic density of states is obtained by the Lorentz expansion of Kohn-Sham eigenvalues. Figure 4 shows the obtained results for the isolated clusters and also for the solids. We can see that the basic features of the density of states for the cluster and solid are almost the same. The small splitting of degenerate states in solid, which is generally propor-

tional to the crystal field, confirms again the very weak interaction between the clusters in  $\text{Al}_{12}\text{C}(\text{Si})$  solid. For the isolated cluster, we have obtained a HOMO-LUMO gap up to 1.96 eV, which is close to the results obtained in the previous calculation by the discrete variational method.<sup>4</sup> In the solid, we find that the change of gap due to the dispersion is small, the obtained energy gap for  $\text{Al}_{12}\text{C}$  solid is 1.52 eV, and for  $\text{Al}_{12}\text{Si}$  is 1.41 eV, which is almost the same as the result obtained for  $\text{C}_{60}$  solid.<sup>3</sup>

To further check the stability of  $\text{Al}_{12}\text{C}$  solid, we have performed a molecular-dynamics simulation at a temperature of  $\sim 20$  K. The simulation is started by giving a small random displacement to each of atoms at the equilibrium structure with a lattice constant of 30.8 a.u. Contrary to the result of fcc-like  $\text{Al}_{12}\text{C}$  (and also  $\text{Al}_{12}\text{Si}$ ) solid,<sup>6,12</sup> we find that the structure of icosahedral  $\text{Al}_{12}\text{C}$  cluster remains unchanged in our observed time of 1.1 ps. The atoms move only around the equilibrium positions. It will also be very interesting to study its dynamical properties and stability changing with temperature, and with pressure, since it may probably have another phase by applying a certain pressure as observed in a typical molecular solid,<sup>20</sup> this work is still in progress.

In conclusion, we have proposed a possible structure for the cluster-assembled  $\text{Al}_{12}\text{C}(\text{Si})$  solid. Based on the first-principles methods, its stability is confirmed by a cohesive

energy, steepest descent on the ions and a dynamical simulation at low temperature. The very small cohesive energy and the small overlap of charge density between clusters suggest that the forces between the  $\text{Al}_{12}\text{C}(\text{Si})$  clusters in the solid phase is van der Waals like. The obtained physical properties for both  $\text{Al}_{12}\text{C}$  solid and  $\text{Al}_{12}\text{Si}$  solid, like electronic structures, are similar to  $\text{C}_{60}$  solid, which indicates that the  $\text{Al}_{12}\text{C}(\text{Si})$  solid might be another interesting cluster-assembled solid. However, since our search in the configuration space is limited, we cannot be sure that this structure for the  $\text{Al}_{12}\text{C}(\text{Si})$  is the most stable. The present studies also show that the shape and geometric structure of the cluster can play an important role in synthesizing a solid, which may bring very rich structures to the cluster-assembled solid.

X.G.G. is thankful to The Third World Academy of Science and CNPq (Brazil) for the hospitality at the CBPF. Thanks are also to Dr. J.A. Helayel-Neto for providing all the facilities that made my stay at CBPF very profitable. This work is partially supported by NNSF of China, and the research developed jointly with National Center of Supercomputation at the Federal University do Rio Grande of Sul (UFRS) and the Center of Supercomputation at the Federal University of Rio de Janeiro (UFRJ), and this work was supported by Sanzhu Co. Ltd. in Shandong.

\*Permanent address: Institute of Solid State Physics, Academia Sinica, 230031 Hefei, China.

<sup>1</sup>*Physics and Chemistry of Finite Systems: From Clusters to Crystal*, edited by P. Jena, S. N. Khanna, and B. K. Rao (Kluwer, Dordrecht, 1992).

<sup>2</sup>H. K. Kroto, *Science* **242**, 1139 (1988); R. L. Whetten *et al.*, The MRS late News Session-Buckeyballs: New Materials Made from Carbon Soot, videotape (Materials Research Society, Pittsburgh, 1990).

<sup>3</sup>Susumu Saito and Atsushi Oshiyama, *Phys. Rev. Lett.* **66**, 2637 (1991).

<sup>4</sup>X. G. Gong and V. Kumar, *Phys. Rev. Lett.* **70**, 2078 (1993); S. N. Khanna and P. Jena, *ibid.* **69**, 1664 (1992).

<sup>5</sup>R. Kawai (unpublished); V. Kumar *et al.* (unpublished).

<sup>6</sup>A. P. Seitsonen, L. Laasonen, R. M. Nieminen, and M. L. Klein, *J. Chem. Phys.* **103**, 8075 (1995).

<sup>7</sup>S. N. Khanna and P. Jena, *Phys. Rev. B* **51**, 13 705 (1995).

<sup>8</sup>J. Q. You, Tianshen Xie, and B. Y. Tang, *Phys. Rev. B* **51**, 1358 (1995).

<sup>9</sup>D. Y. Sun and X. G. Gong, *Phys. Rev. B* **54**, 17 051 (1996).

<sup>10</sup>D. P. Shoemaker *et al.*, *Acta Crystallogr.* **5**, 637 (1952); H. Ido, J.

C. Sohn, P. Pourarian, S. F. Cheng, and W. E. Wallace, *J. Appl. Phys.* **67**, 4978 (1990).

<sup>11</sup>G. W. Zhang, X. G. Gong, and Q. Q. Zheng, *J. Appl. Phys.* **76**, 7037 (1994).

<sup>12</sup>A. P. Seitsonen, M. J. Puska, M. Alatalo, and R. M. Nieminen, *Phys. Rev. B* **48**, 1981 (1993).

<sup>13</sup>S. N. Khanna and P. Jena, *Chem. Phys. Lett.* **219**, 479 (1994).

<sup>14</sup>F. Liu, M. Mostoller, T. Kaplan, S. N. Khanna, and P. Jena, *Chem. Phys. Lett.* **248**, 213 (1996).

<sup>15</sup>J. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).

<sup>16</sup>R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

<sup>17</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

<sup>18</sup>G. B. Bachelet, D. R. Hamann, and M. Schluter, *Phys. Rev. B* **26**, 4199 (1982).

<sup>19</sup>H. P. Chen, R. S. Berry, and R. L. Whetten, *Phys. Rev. B* **43**, 10 647 (1991); J. Y. Yi, D. J. Oh, J. Bernholc, and R. Car, *Chem. Phys. Lett.* **174**, 461 (1990).

<sup>20</sup>M. Benoit, M. Bernasconi, P. Focher, and M. Parrinello, *Phys. Rev. Lett.* **70**, 2934 (1996).