

## A tight-binding molecular dynamics study of $\text{Ni}_m\text{Si}_n$ binary clusters

Antonios N. Andriotis<sup>a,1</sup>, Madhu Menon<sup>b,c,2</sup>, George E. Froudakis<sup>d</sup>,  
Zacharias Fthenakis<sup>e</sup>, J.E. Lowther<sup>f</sup>

<sup>a</sup> *Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, 71110 Heraklio, Crete, Greece*

<sup>b</sup> *Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055, USA*

<sup>c</sup> *Center for Computational Sciences, University of Kentucky, Lexington, KY 40506-0045, USA*

<sup>d</sup> *Department of Chemistry, University of Crete, P.O. Box 1470, 71409 Heraklio, Crete, Greece*

<sup>e</sup> *Department of Physics, University of Crete, P.O. Box 1470, 71409 Heraklio, Crete, Greece*

<sup>f</sup> *Physics Department, University of the Witwatersrand, 1 Jan Smuts Avenue, Johannesburg, South Africa*

Received 13 April 1998; in final form 1 June 1998

### Abstract

A transferable tight-binding parametrization of the Ni–Si interactions, from small binary  $\text{Ni}_m\text{Si}_n$  clusters to bulk  $\text{NiSi}_2$ , is presented within a minimal parameter basis. The data base for fitting the parameters is obtained from (i) ab initio results for the NiSi dimer obtained using the density functional method and the single, double and triple coupled clusters method, and (ii) band structure results for the bulk  $\text{NiSi}_2$ . The parametrization is incorporated into the tight-binding molecular dynamics scheme to study medium size  $\text{Ni}_m\text{Si}_n$  clusters. Our results are in very good agreement with experiment. © 1998 Published by Elsevier Science B.V. All rights reserved.

Metal-semiconductor interfaces and, in particular, transition metal silicides (TMS's) grown on Si surfaces have attracted major research interest due to their technological importance in semiconductor fabrication. An attractive feature is that they exhibit abrupt interfaces and very low sheet resistance. Furthermore, transition-metal silicides offer high temperature materials for Si metalization as well as rectifying junctions with a variety of Schottky barrier heights (SBH's). Also, transition metal silicides (and

in particular  $\text{NiSi}_2$  and  $\text{CoSi}_2$ ) constitute prototype systems in surface science studies for understanding the effect of the transition metal atoms in surface reconstruction and hetero-diffusion. However, despite intense research efforts, the growth mechanism of metal silicides on Si has not yet been completely understood. Thus, the epitaxially grown  $\text{NiSi}_2$  on Si(111) and Si(100) surfaces exhibits SBH's which depend not only on the substrate orientation but also on the growth conditions [1–3]. It has been shown that the different SBH's measured for  $\text{NiSi}_2$  reveal various local structural interface variations which are associated with various degrees of interfacial reconstructions [1,2]. Furthermore, the problem of  $\text{NiSi}_2$

<sup>1</sup> E-mail: andriot@iesl.forth.gr

<sup>2</sup> E-mail: super250@convex.uky.edu

(or  $\text{CoSi}_2$ ) growth on Si surfaces poses a number of questions that have not been answered yet. For example, the nature and the identification of the initial (nucleation) sites for Ni(Co) on the Si surfaces and their subsequent evolution into forming silicide compounds as well as the observed [1] multiple phase structures of the  $\text{NiSi}_2$  during its growth on Si(100), constitutes some of the most important questions that have been the focus of intense theoretical and experimental interest recently.

Experimentally, the key factors controlling the initial stages of growth of  $\text{NiSi}_2$  on Si substrate appear to be the misfit between the silicide and the Si substrate as well as the diffusion rate of Ni into Si and that of Si into Ni. The theoretical calculations (performed at  $T = 0$ ), however, appear to be inadequate in supporting the experiments which indicated an increased tendency for Ni to diffuse into Si. Theoretical results indicate that at  $T = 0$  the diffusion of Ni into Si is not favorable (or at least the activation energy for diffusion is too large). The diffusion mechanism, therefore, is thought to be assisted by the presence of surface defects and/or the elevated substrate temperature at which experiments are performed.

The use of the scanning tunneling microscope (STM) has helped in identifying the most stable sites for Co and Ni nucleation on Si surfaces [4,5]. In particular, Co atoms have been found to indiffuse into the Si(111)-(7 $\times$ 7) substrate occupying a position close to a subsurface interstitial site without affecting the surface reconstruction; these sites were proposed as precursors to silicide formation [4]. Similar behavior has also been suggested for Ni atoms on Si surfaces [4]. Also, STM pictures have shown the formation of a Ni-induced (2 $\times$ 1) surface structure during the initial growth of Ni on Si(100) [1,6]. Other experimental findings have suggested that it is possible for the initially formed Ni clusters to react with the Si surface, releasing sufficient energy to promote Si atoms over the Ni clusters suggesting, thus, a possible mechanism for silicide formation [7,8]. Such a mechanism was proposed earlier by Zunger [9] for the case of Al clusters grown on GaAs.

The theoretical investigations of the Si–silicide interfaces are usually based on band structure calculations applied on various slab geometries, the latter

used to model the Si–silicide interfaces [3,5,10–14]. Some cluster calculations have also been reported for modeling the  $\text{CoSi}_2/\text{Si}(111)$  and  $\text{NiSi}_2/\text{Si}(111)$  interfaces [15]. All these calculations have been performed using either the density functional theory (DFT) within the local density approximation (LDA) or the tight-binding (TB) scheme. There appears to be a noticeable preference for the TB calculational schemes because of the computational complexity associated with large scale calculations of the Si–silicide interface with ab initio methods. Also, to the best of our knowledge, ab initio calculations at the configuration interaction (CI) level have not been reported for the Ni–Si system. This is mainly due to the calculational difficulties associated with the Ni species even in its free atom state. In particular, Ni exhibits sensitivity to the electron correlation effects (due to its open *d*-shells) and the results depend strongly on the CI-level used, (see for example, discussions in Ref. [16]).

In this Letter, we report on results derived from a theoretical investigation of the binary  $\text{Ni}_m\text{Si}_n$  clusters using the tight-binding molecular dynamics (TBMD) scheme based on data obtained from ab initio calculations. Our approach is an application of the TBMD calculational scheme as used earlier in our studies of covalent and metallic systems. The successful applications of the TBMD method in the studies of clusters of both semiconductor [17] and transition metal atoms [16,18–20] allow us to draw useful conclusions from studies of more complex systems such as the large binary clusters of  $\text{Ni}_m\text{Si}_n$  which, at the present, are beyond the domain of ab initio theories. Our approach allows us to perform both symmetry unconstrained and spin unrestricted optimizations simultaneously for the determination of the ground state geometry of the binary cluster in a computationally efficient manner. The TBMD scheme employed [16,18–20] is semi-empirical and requires only a minimal number of fitting parameters which include the experimental or the theoretical bond lengths and the vibrational frequencies of the dimers  $\text{Si}_2$ ,  $\text{Ni}_2$  and  $\text{NiSi}$  as well as the ab initio total energy results of small  $\text{Ni}_m\text{Si}_n$  clusters with  $n + m < 4$ . The fitting parameters include (i) the strength  $\phi_0^{A-B}$  of the pair repulsive interaction between A and B atoms,  $A, B = \text{Si}, \text{Ni}$ , and (ii) the scaling factor,  $\alpha_{A-B}$ , for the distance dependence of

Table 1

Results for the dimers  $\text{Si}_2$ ,  $\text{Ni}_2$  and  $\text{NiSi}$  obtained using ab initio methods in the present work

Dimer	State	Bond length (Å)		Vibration frequency ( $\text{cm}^{-1}$ )			
$\text{Si}_2$	$^3\Sigma_g^-$	2.286 <sup>a</sup>	2.271 <sup>b</sup>	2.246exp <sup>c</sup>	481 <sup>a</sup>	492 <sup>b</sup>	511 exp <sup>c</sup>
$\text{Ni}_2$	$^3\Sigma_u^+$	2.239 <sup>a</sup>	2.249 <sup>b</sup>	2.20exp <sup>d</sup>	292 <sup>a</sup>		330exp <sup>d</sup>
$\text{NiSi}$	$\dots\sigma_g^2\pi^4\delta^2$	2.142 <sup>a</sup>	2.124 <sup>b</sup>		400 <sup>a</sup>		

Experimental and other theoretical results are also shown for comparison. <sup>a</sup> Results obtained with the DFT method. <sup>b</sup> Results obtained with the CCSD(T) method. <sup>c</sup> As quoted in Refs. [26,27]. <sup>d</sup> See for example Ref. [20] and references therein.

the interaction parameters for the interaction between A and B atoms (A,B = Si,Ni). The details of our method, as applied to pure clusters, can be found elsewhere [16,18–20].

It must be emphasized that our fitting parameters for Si and Ni are the same as those used in our independent studies of pure  $\text{Si}_n$  and  $\text{Ni}_n$  clusters. The difficulty arises in finding adequate data to fit the parameters that describe the Si–Ni interaction. Since, to the best of our knowledge, neither theoretical nor experimental results have been reported for the NiSi dimer, we had to perform a series of ab initio calculations for the NiSi dimer. In particular, the bond length  $r_{\text{NiSi}}$  and the vibrational frequency,  $\omega_{\text{NiSi}}$ , of the NiSi dimer are taken from a binding energy curve obtained within the density functional theory (DFT) and the single, double and triple coupled-clusters method (CCSD(T)) [21]. All calculations were carried out using the GAUSSIAN 94 program package [22]. For the DFT method, the three-parameter hybrid functional of Becke [23] using the Lee-Yang-Parr correlation functional [24], (B3LYP), was employed for the geometry optimizations and for the vibrational frequency calculations. The atomic basis set includes Gaussian functions of triple zeta quality augmented by  $d$  polarization functions (6-311G\*) [22]. For both, DFT and CCSD(T) methods we used atomic basis sets which included Gaussian functions of triple zeta quality augmented by  $d$  polarization functions (6-311G\*) [22]. The bonding features of the optimized structures were investigated by Mulliken population analysis [25]. The results of our calculations are included in Table 1.

For our fitting purposes we used the experimental results for  $\text{Si}_2$  and  $\text{Ni}_2$ . Towards this end we scaled our ab initio results for the NiSi dimer accordingly. Thus, for the fitting purposes we take  $r_{\text{NiSi}} = 2.10 \text{ \AA}$

and  $\omega_{\text{NiSi}} = 436 \text{ cm}^{-1}$ . It should be noted, however, that the binding energy curve alone is not sufficient to determine the parameters for the Ni–Si interaction accurately. It is also necessary for the fitted parameters to reproduce the charge transfer obtained by the ab initio calculations for the Ni–Si dimer. In our case this is achieved by trial and error by adjusting the diagonal tight-binding matrix elements of Ni until the correct charge transfer is obtained (approximately 0.25 electrons gained by Si from Ni at the equilibrium bond length<sup>3</sup>).

For the off-diagonal matrix elements describing the Ni–Si interaction, we used the results of Robertson [11] in order to fit the parameter  $r_d$  in terms of which (and the universal parameters) the  $sp-d$  interactions of the Ni–Si bond are described [28]. The ab initio data for the dimers used in fitting our parameters is shown in Table 1. The resulting parameter values for  $r_d$ ,  $\phi_0^{A-B}$  and  $\alpha_{A-B}$ , A,B = Si,Ni are shown in Table 2.

Additionally, in order to correctly describe the bulk  $\text{NiSi}_2$ , we included a correction term in the diagonal tight-binding matrix elements which could take into account the local environment of each cluster-atom. The correction term was obtained by interpolating dimer values (as obtained from our fitting process) and bulk values [11] linearly with respect to unlike neighbors of each atom.

Sufficient tests were carried out to ensure satisfactory description of the Ni–Si interactions in various

<sup>3</sup> The problem of the theoretical determination of the charge transfer in the NiSi dimer needs some attention as it depends strongly on the level of approximation used. For example, Hartree-Fock calculations or/and closed shell electron configurations lead to opposite value for the charge transfer, (i.e., indicating Si losing electrons to Ni), compared to the results of the DFT and the CCSD (T) methods used in the present work.

Table 2

Fitted constants  $\phi_0^{A-B}$ ,  $\alpha_{A-B}$  and the parameter  $r_d$  for the interactions between A and B atoms, A,B = Si,Ni

A–B	$\phi_0^{A-B}$ (eV)	$\alpha_{A-B}$ ( $\text{\AA}^{-1}$ )	$r_d$ ( $\text{\AA}$ )
Si–Si	2.693	0.574	
Ni–Ni	0.264	1.040	0.71 [28]
Ni–Si	0.745	0.790	1.0145 <sup>a</sup>

<sup>a</sup> As obtained by fitting to the TB parameters given by Robertson [11]

(local) environments in terms of Harrison's universal off-diagonal matrix elements in conjunction with our choice for the diagonal matrix elements and the fitted parameters. Indeed, our calculations reproduced both the bulk Ni, Si and NiSi<sub>2</sub> band structures as well as the ab initio results for the trimers Ni<sub>2</sub>Si and Si<sub>2</sub>Ni satisfactorily. This ensures that our tight-binding parametrization describes in a very satisfactory way the limiting cases of all the dimers and bulk type of environments that may appear in the various configurations of the binary Ni<sub>m</sub>Si<sub>n</sub> clusters. Therefore, it allows us to expect that, within this parametrization, intermediate cases will be suitably described.

We next present our results for Ni<sub>m</sub>Si<sub>n</sub> with  $n + m \geq 4$ . The choice of initial configurations were guided by our prior experience with pure Ni and Si cluster ground state geometries. We then substituted some of the atoms with atoms belonging to a different chemical species to create binary clusters. Molec-

ular dynamics is then performed to determine the optimized geometry.

Application of the present method to the tetramers Ni<sub>2</sub>Si<sub>2</sub> confirms the validity of the choice of parameters. Fully relaxed geometries of three tetramers T1, T2 and T3 are shown in Fig. 1a, Fig. 1b and Fig. 1c, respectively. Simple arguments based on the relative strengths of the bond energies  $\epsilon_{A-B}$  of the dimers A–B, A,B = Si,Ni, for which our ab initio calculations confirm that

$$\epsilon_{\text{Si-Si}} > \epsilon_{\text{Ni-Si}} > \epsilon_{\text{Ni-Ni}}, \quad (1)$$

implying that (for clusters of the same geometry and magnetic moment) structures with Si–Si bonds will tend to be more stable. Indeed, our calculations show geometry T3 to be most stable followed by T2. We find the pyramidal structure T3 to be 1.776 eV more stable than T1 and 1.602 eV more stable than T2. It should be noted, however, that only T1 is magnetic (with two electrons more in the majority spin-state) while all the other relaxed geometries are found to be non-magnetic. We also considered a rhombus structure for the tetramer with a Ni–Ni bond forming the short diagonal (obtained by switching Si with Ni in T2). The molecular dynamics relaxation for this cluster turned it into the geometry of T2.

Relaxed geometries for two pentamers P1 and P2 of the Ni<sub>2</sub>Si<sub>3</sub> are shown in Fig. 2a and Fig. 2b, respectively. The P1 cluster has the geometry of a trigonal bipyramid, while P2 is a square pyramid.

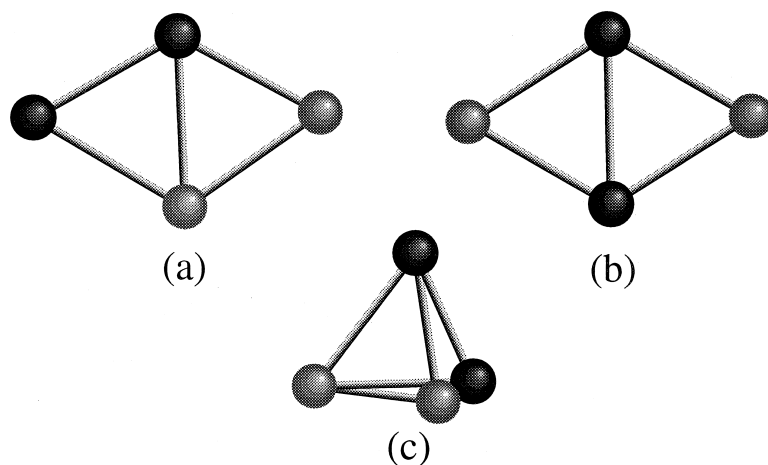


Fig. 1. Stable Ni<sub>2</sub>Si<sub>2</sub> tetramer clusters; (a) T1, (b) T2 and (c) T3. Si atoms are shown in dark.

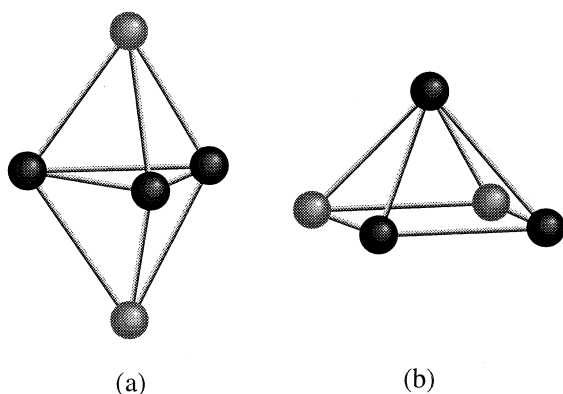


Fig. 2. The relaxed (a) P1 and (b) P2 geometries of two  $\text{Ni}_2\text{Si}_3$  pentamers (see text). Dark (light) colored spheres indicate Si (Ni) atoms.

Both these structures were found magnetic (with two electrons more in the majority spin-state). From Fig. 2 it can be seen that one of the Si atoms in both P1 and P2 have the same neighbor environment. In P1, each of the other two Si and two Ni atoms exhibit one more Ni–Si bond than the corresponding atoms in the P2 geometry. P2 geometry is found to be

1.434 eV more stable than P1 (contrary to the expectation following previous arguments based on Eq. (1)). One can surmise that the presence of Ni atoms weakens the Si–Si bonds substantially. In terms of our parametrization, this is the result of the dependence of the diagonal Hamiltonian matrix elements on the local environment of each atom (i.e., coordination number and number of unlike neighbors), that has been implemented in our model. These results are consistent with the experimental findings which gave evidence that the presence of Ni atoms in Si does indeed weaken the Si–Si bonds [29–32].

We next present our results for larger  $\text{Ni}_m\text{Si}_n$  clusters. The aim of the study of larger clusters is to provide answers to some of the Si–silicide interface problems referred earlier in this Letter. In particular, we explore the effects of the presence of Ni atoms in mainly a Si environment (surface or bulk) and vice versa. In Fig. 3a we show a fully relaxed  $\text{Ni}_{34}\text{Si}_5$  cluster. It represents the effects of substitutional Si atoms on a Ni fcc surface. The initial configuration in the molecular dynamics did not change appreciably on Si substitution indicating that the effect is

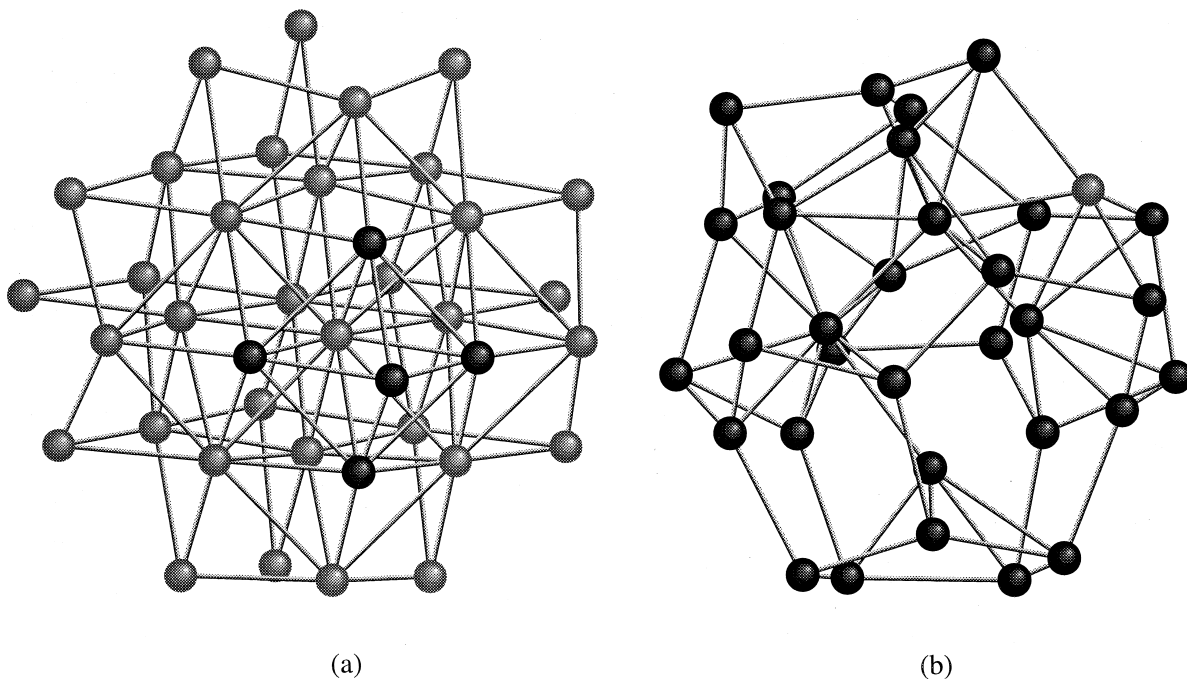


Fig. 3. Relaxed geometries of the (a)  $\text{Ni}_{34}\text{Si}_5$  and (b)  $\text{Si}_{32}\text{Ni}$  clusters.

minimal. The final results for substitutional Ni atom on predominantly Si cluster (Fig. 3b), however, is drastically different from the initial configuration. In this Si<sub>32</sub>Ni cluster, the presence of a Ni atom induces severe changes in a Si host as the Ni atom tries to make more bonds with the surrounding atoms. All these results are consistent with the experimental findings.

In conclusion, we have obtained ab initio results for the Ni–Si dimer which we then used for a parametrization of the Ni–Si interaction within a TB scheme. This parametrization was further implemented in our TBMD code that was used to study the dynamics of the Ni atoms in a Si environment and vice versa. Our results are in good agreement with the experimental findings, confirming the validity of our approach which can be used in system sizes beyond the reach of ab initio methods.

### Acknowledgements

The present work is supported by the NATO grant CRG 970018, by NSF grant OSR 94-52895, and by the University of Kentucky Center for Computational Sciences.

### References

- [1] Y. Khang, Y. Kuk, Phys. Rev. B 53 (1996) 10775.
- [2] R.T. Tung, A.F.J. Levi, J.P. Sullivan, F. Schrey, Phys. Rev. Lett. 66 (1991) 72.
- [3] G.P. Das, P. Blochl, O.K. Andersen, N.E. Christensen, O. Gunnarsson, Phys. Rev. Lett. 63 (1989) 1168.
- [4] P.A. Bennett, D.G. Cahill, M. Copel, Phys. Rev. Lett. 73 (1994) 452.
- [5] B. Voigtlander, V. Scheuch, H.P. Bonzel, S. Heinze, S. Blugel, Phys. Rev. B 55 (1997) R13444.
- [6] D. Loretto, J.M. Gibson, S.M. Yalisove, Phys. Rev. Lett. 63 (1989) 298.
- [7] E.J. van Loenen, J.F. van der Veen, Surf. Sci. 157 (1986) 1.
- [8] D. Mangelinck, P. Gas, A. Grob, B. Pichaud, O. Thomas, J. Appl. Phys. 79 (1996) 4078.
- [9] A. Zunger, Phys. Rev. B 24 (1981) 4272.
- [10] D.R. Hamann, L.F. Mattheiss, Phys. Rev. Lett. 54 (1985) 2517.
- [11] J. Robertson, J. Phys. C: Solid State Phys. 18 (1985) 947.
- [12] O. Bisi, L.W. Chiao, K.N. Tu, Phys. Rev. B 30 (1984) 4664.
- [13] J.T. Schick, S.M. Bose, Phys. Rev. B 53 (1996) 12609.
- [14] X. Yongnian, Z. Kaiming, X. Xide, Phys. Rev. B 33 (1986) 8602.
- [15] P.J. van den Hoek, W. Ravenek, E.J. Baerends, Phys. Rev. Lett. 60 (1988) 1743.
- [16] N.N. Lathiotakis, A.N. Andriotis, M. Menon, J. Connolly, J. Chem. Phys. 104 (1996) 992.
- [17] M. Menon, R.E. Allen, Phys. Rev. B 38 (1988) 6196.
- [18] A.N. Andriotis, N. Lathiotakis, M. Menon, Chem. Phys. Lett. 260 (1996) 15.
- [19] Menon, N. Lathiotakis, A.N. Andriotis, Phys. Rev. B 56 (1997) 1412.
- [20] A.N. Andriotis, M. Menon, Phys. Rev. B 57 (1998) 10069.
- [21] J.A. Pople, M. Head-Gordon, K. Raghavachari, J. Chem. Phys. 87 (1987) 5968.
- [22] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. DeFrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision D.4, Gaussian, Pittsburgh, PA, 1995.
- [23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [24] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [25] R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833.
- [26] K. Raghavachari, J. Chem. Phys. 84 (1986) 5672.
- [27] P.J. Bruna, S.D. Peyerimhoff, R.J. Buenker, J. Chem. Phys. 72 (1980) 5437.
- [28] W. Harrison, in: Electronic Structure and Properties of Solids (W.H. Freeman, San Francisco, CA, 1980).
- [29] K.N. Tu, Appl. Phys. Lett. 27 (1975) 221.
- [30] N.W. Cheung, J.W. Mayer, Phys. Rev. Lett. 46 (1981) 671.
- [31] F. Comin, J.E. Rowe, P.H. Citrin, Phys. Rev. Lett. 51 (1983) 2402.
- [32] Y.J. Chang, J.L. Erskine, Phys. Rev. B 26 (1982) 4766; B 26 (1982) 7031.