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# Metal-coated fullerenes: electronic, geometrical and vibrational properties of $C_{60}M_{62}$ (M = Ti and V)

M.R. Pederson [a,*], D.V. Porezag [b], D.C. Patton [a], Efthimios Kaxiras [c]

[a] Complex Systems Theory Branch – 6692, Naval Research Laboratory, Washington, DC 20375-5000, USA
[b] Department of Physics, Georgetown University, Washington, DC 20057, USA
[c] Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

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## Abstract

Recent experiments have revealed well-defined magic numbers for transition-metal-coated fullerenes $C_{60}M_N$ (for example, M = Ti, V, Zr, and $N = 50$, 62, 72, 80). We investigate the origin of the stability of such metal-coated fullerenes through first-principles calculations and compare these structures to other forms of clusters containing C and transition metals. Although, the transition-metal coatings disrupt the $\pi$ bonding on the fullerene cage, we find that the clusters should be metastable at low temperatures or laser fluence. We discuss relative stabilities, the electronic and vibrational propertries, and the nature of bonding in the representative $C_{60}Ti_{62}$ cluster. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The discovery of the $C_{60}$ (fullerene) molecule and forms related to it (other smaller or larger fullerenes, tubes, concentric shells, etc.) has led to intense investigations of these systems. Of particular interest are forms that could combine the inert, insulating behavior of the $C_{60}$ molecule with other atoms or molecules, possibly giving it new physical and chemical properties. Early efforts concentrated on the production of $C_{60}$ or related molecules, such as $C_{28}$, with other atoms inside them [1–3]. More recent work identified fullerenes which are coated by a layer of metal atoms [4–6]. The remarkable ability of the fullerenes to form stable structures by either enclosing, or being enclosed by, other atoms has given rise to hopes that these structures can be useful in practical applications. In most cases, however, the structural, electronic and thermal properties of these structures remain poorly understood. The lack of understanding is due partly to the novelty of the physical systems and partly to the difficulty of studying them by conventional structural analysis methods (such as scattering of electrons or X-rays).

The recent mass-spectrographic studies by Tast et al. on transition-metal-coated fullerenes ($C_{60}M_N$) revealed sharp peaks at $N = 62$ for Ti, V and Zr coatings [5]. While $N = 62$ is common to all three transition metals, Ti and Zr exhibit additional peaks in the mass spectra at $N = 50$, 72 and 80, and V exhibits peaks at $N = 73$ and 86. Magic alkaline-earth-coated fullerenes, with $N = 32$, 35, 38 and 43, have already been thoroughly investigated [4]. Arguments based on atomic packing and the ratio of transition-metal/alkaline-earth atomic radii suggest

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[*] Corresponding author. E-mail: pederson@dave.nrl.navy.mil

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that a monolayer of Ti and Zr on $C_{60}$ would consist of approximately 58–77 atoms [6]. While simple packing arguments are instructive, they are insufficient to predict the stable structures because the magic numbers are often determined by electronic or atomic shell closings [6]. On the other hand, the preferred valence and coordination numbers of transition metals depends on their environment, and therefore the precise magic numbers of clusters may not be determined by shell closing alone. Indeed, the doubly and singly ionized $C_{60}M_N$ mass spectra exhibit the same peaks suggesting that the peaks are not due exclusively to electronic shell closings.

In the present Letter we hypothesize that the peaks in the mass spectra of metal-coated fullerenes are associated with highly symmetric clusters which preserve the icosahedral symmetry of the fullerene, and are consistent with close packing of the metal atoms. We base this hypothesis on the following observations: The icosahedral symmetry of the fullerene molecule can be maintained by placing a shell of $n_1 = 12$ atoms above the pentagonal faces, a shell of $n_2 = 20$ atoms above each of the hexagonal faces, a shell of $n_3 = 30$ atoms above each of the hexagon–hexagon carbon bonds or a shell of $n_4 = 60$ atoms above each of the carbon atoms in $C_{60}$. On symmetry grounds alone one would expect that magic numbers could appear for any number $N = \Sigma_i p_i \times n_i$ with $p_i$ an integer. Candidates for magic numbers which are in the range suggested by packing arguments, are given by $N = 50$ (with $p_2 = p_3 = 1$), 62 (with $p_1 = p_2 = p_3 = 1$), 72 (with $p_1 = p_4 = 1$), and 80 (with $p_2 = p_4 = 1$). It is intriguing that these numbers coincide exactly with the Ti and Zr mass-spectra peaks and the $N = 62$ mass-spectra peak for V that have been observed by Martin et al. [5,6]. Smaller candidates ($N = 12$, 20, 30 and 32) are expected to be reactive (hence less stable and more difficult to observe), since packing arguments suggest that there is enough room for additional transition metal atoms. Further evidence for a balance between high-symmetry and packing considerations is provided by the behavior of the mass-spectra peak for size $N = 50$, as a function of transition-metal radius: Zr, which has the largest radius, exhibits a strong peak while Ti, which has a smaller radius, exhibits a shoulder and V, with the smallest radius, exhibits no spectral weight at all [6] at this size.

## 2. Computational details

To quantify our hypothesis and determine the physical and chemical properties of transition-metal-coated fullerenes we use the Naval Research Laboratory Molecular Orbital Library (NRLMOL) [7,8] to perform state-of-the-art density functional theory (DFT) calculations. Recent extensions of NRLMOL allow for the use of pseudopotentials [9] and for massively parallel calculations [10]. The calculations discussed here were performed on a four-processor SGI Origin 2000. Despite the improvements in computational capabilities offered by our codes, calculations for these systems remain rather demanding. We have therefore concentrated on one cluster size, namely the $C_{60}M_{62}$, with M = Ti, V. We believe the study of this cluster reveals most of the essential features of the metal-coated fullerenes, with other stable sizes exhibiting similar (if slightly different due to different size) behavior. The studies of Ti/C clusters were performed with the all-electron option, using the PW91 functional for the generalized gradient approximation [11,12]. For these calculations we used 12 optimized bare gaussians to construct a (5s,4p,3d) contracted orbital set for C and 19 optimized bare gaussians to construct a (7s,5p,4d) contracted orbital set for Ti. Additional work on the V/C clusters was performed with pseudopotentials. For the pseudoatoms of C and V we used a 6 gaussian (4s,4p,3d) basis set and an 8 gaussian (4s,3p,2d) basis set, respectively [1]. We analyze next the geometrical structure, the electronic structure and the nature of bonding in representative metal-coated fullerenes.

## 3. Results

### 3.1. Geometrical structure

In Fig. 1 we show the equilibrium geometry for the icosahedral $C_{60}Ti_{62}$ cluster as obtained by mini-

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[1] Electronic copies of the basis sets are available from the authors upon request. For additional information see Ref. [13]. Basis sets are available at http://archiv.tu-chemnitz.de/pub/1997/0025.

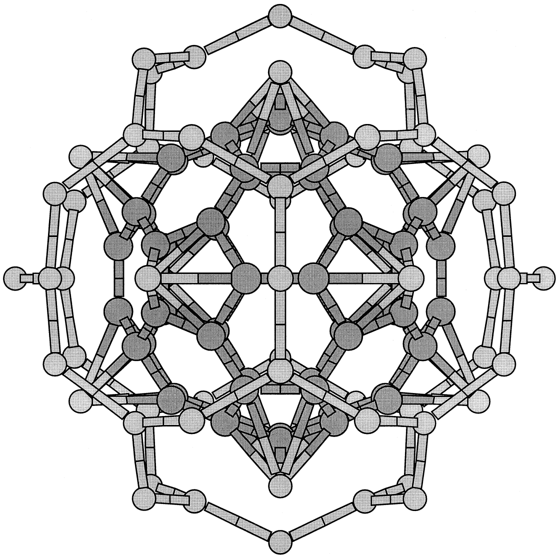

Fig. 1. Structure of the Ti-coated $C_{60}Ti_{62}$ cluster. Darker spheres represent C atoms, lighter spheres Ti atoms.

mizing the energy of the system [2]. The cluster is constructed by placing a carbon atom at (0.000, 3.6285, 0.7583) Å, and three inequivalent Ti atoms at (0.000, 4.4800, 2.7689) Å, (0.000,0.000,5.9620) Å, and (3.1083, 3.1083, 3.1083) Å, respectively. The remaining atoms are generated from the icosahedral symmetry operations. For the relaxed structure, the hexagon–hexagon and pentagon–hexagon bond lengths are found to be 1.516 and 1.484 Å, respectively, which are significantly stretched in comparison to the corresponding bond lengths in the isolated fullerene and very close to C–C bond lengths associated with 4-fold coordinated carbon atoms (e.g., the C–C bond lengths in diamond and ethane are approximately 1.53 Å). Increased bond lengths are indicative of a disruption of the hexagon–hexagon $\pi$ bonding on the fullerene cage. The mechanism for this is discussed below. The 12 Ti atoms above the pentagonal rings are bonded to the C atoms with a bondlength of 2.184 Å and the remaining 50 Ti atoms form a closed outer cage consisting of 12 buckled decagons with Ti–Ti bond lengths of 2.125 Å. The Ti atoms form a bilayer with 30 Ti atoms situated 5.96 Å away from the fullerene center and 12 pentagonal and 20 hexagonal Ti atoms situated 5.27–5.38 Å away from the fullerene center.

### 3.2. Electronic structure

A study of the electronic structure of this system reveals that it has no gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). At the Fermi level there are three accidentally degenerate representations with $T_{2u}$, $T_{1u}$ and $H_g$ symmetry, respectively. Including spin, a total of two electrons occupy these 22 degenerate levels. The Hubbard $U$ is 1.87 eV, the electron affinity is $-2.28$ eV, and the first and second ionization energies are 4.15 and 10.18 eV. For comparison, the calculated (experimental) numbers for $C_{60}$ are: Hubbard $U = 3.04$ eV, electron affinity is 2.89 (2.74) eV, and first ionization energy is 7.9 (7.6) eV [14]. The chemical hardness is reduced in comparison to the isolated $C_{60}$ molecule indicating that the Ti-coated clusters are significantly more reactive. Our calculation which finds an open-shell structure is in accord with the experimental results of Tast et al. which find similar mass spectra for both $+1$ and $+2$ charge states of $C_{60}Ti_{62}$ [6]. Similar mass spectra for the negatively charged states would be expected as well. Close examination of the Ti-d and C-p density of states, shows that the states near the Fermi level consist of an admixture of Ti-3d and C-2p character.

### 3.3. Nature of bonding

Bonding in this cluster is an intersting combination of ionic and covalent character. The C–Ti bonding is not entirely covalent and the charge states of the three types of Ti are not the same. Within

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[2] The rms residual forces on the atoms are smaller than 0.025 eV/Å, which is well below the accepted limit for well converged geometry optimization. The largest force on any atom is 0.07 eV/Å. Reducing the forces to this level from the typical convergence criterion of 0.1 eV/Å decreases the total energy by approximately 0.01 eV. The symmetry constraints imposed produce structures with smaller forces than in the absence of any constraint. When we relax the symmetry constraints and allow for Jahn–Teller distortions we find that the symmetry is hardly broken.

non-overlapping spheres of radius 2.0 bohr, the pentagonal, hexagonal and bond-centered Ti atoms have electronic charges of 19.6, 19.8 and 20.0, respectively. For comparison, a 2.0 bohr sphere centered about an isolated Ti atom would capture 19.9 units of charge. Non-overlapping spheres of 1.32 bohr placed about the C atoms contain a total of 3.99 units of charge in $C_{60}Ti_{62}$ and 3.92 units of charge in an isolated $C_{60}$ molecule with the same geometry. When an additional 12 electrons are added to this isolated geometry (using the neutral unoccupied $T_{1u}$ and $T_{1g}$ Kohn–Sham orbitals), the same sphere captures 4.02 units of charge. This analysis suggests that the fullerene molecule accepts a total of 12 electrons from the 12 pentagonal Ti atoms and that in addition to some covalent bonding there is ionic bonding between the pentagonal Ti atoms and the fullerene cage.

To understand further the bonding between the pentagonal Ti atoms and the fullerene pentagons it is instructive to consider the bonding between a single Ti and a $C_5H_5$ ring (cyclopentadienyl). The isolated molecule consists of a pentagon of C atoms each of which forms a $\sigma$ bond with a H atom (1.09 Å) and two other C atoms (1.41 Å). Because of the five-membered ring the system is frustrated but $\pi$ bonding is introduced as a result of Jahn–Teller distortions. These distortions can be supressed if the $C_5H_5$ ring molecule captures an additional electron. We have performed electronic structure calculations on $C_5H_5$ and $C_5H_5Ti$ and have verified that when a Ti atom is placed on the face of a $C_5H_5$ ring the Ti atom donates one electron to the pentagon. For $C_5H_5$, the bonding between the Ti atoms and the ring is primarily ionic with the Ti 3d states contributing to the HOMO and LUMO states. To understand the interaction between the hexagonal Ti atoms and the fullerene hexagons we have performed similar calculations. In contrast to the pentagonal case, a hexagonal ring of three-fold coordinated carbon atoms has a closed-shell electronic structure, for bond lengths in the 1.30–1.60 Å range. Accordingly, charge transfer from Ti atoms to the hexagonal ring is not required for maintaining a $\sigma$ bonded fullerene shell.

To summarize the above discussion of bonding, the pentagonal Ti atoms play the key role in causing the fullerene cage to relax. The donation of charge to the pentagonal fullerene rings reduces their frustration and alleviates the need for the formation of hexagon–hexagon $\pi$ bonds in the fullerene. Upon removal of the hexagon-hexagon $\pi$ bonds the fullerene cage relaxes to a geometry which is more consistent with C–C single bonds. To illustrate these points, we show in Fig. 2 the charge density of the metal-coated fullerene. The distribution of valence charge indicates that there is covalent bonding between the hexagonal and bond-centered Ti atoms and, to a lesser extent, between the C atoms and the pentagonal Ti atoms. The bond-centered and hexagonal Ti atoms form a network of covalently bonded atoms, which would be broken upon removal of one of these atoms. Thus, the structure can be thought of as composed of the fullerene cage with the 12 pentagonal Ti atoms attached to it by mixed ionic and covalent bonding, plus the network of the 50 covalently bonded bond-centered and hexagonal Ti atoms which fits nicely around the carbon cage. The stability of this network leads us to suggest that a similar structure with 50 metal atoms around the $C_{60}$ cage corresponds to the structure of the $C_{60}M_{50}$ clusters.

### 3.4. Relative stability

In order to compare the stability of the $C_{60}Ti_{62}$ cluster to other low-energy configurations, we have

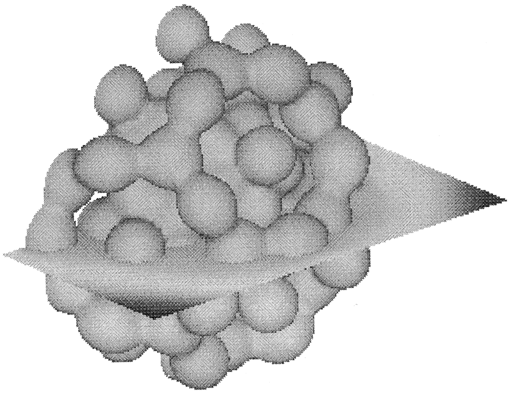

Fig. 2. Plot of the valence charge density of $C_{60}Ti_{62}$. The contour shows that the bond-centered and hexagonal Ti atoms form a closed outer cage of Ti atoms which exhibit covalent Ti–Ti bonding. While the bonding between the pentagonal Ti atoms and the fullerene cage is primarily ionic, the pentagonal Ti atoms show a greater propensity for covalent Ti–C bonding than the other Ti atoms.

performed all-electron calculations on two rock-salt fragments ($C_{32}Ti_{32}$ and $C_4Ti_4$) and a $C_{12}Ti_8$ METCAR structure that was originally discovered by Guo and coworkers [15–17] [3]. The geometry of all structures has been optimized. Since the METCAR and the coated fullerene do not have a 1:1 stoichiometry between Ti and C we have added the energy of an appropriate number of Ti and C atoms from the relevant atomic reservoirs (4 Ti bulk atoms and 2 C graphite atoms). The energies of atoms in these reservoirs were taken from similar calculations [4]. The results are summarized in Table 1. While the quantitative energies per pair of TiC atoms are weakly dependent on the choice of atomic reservoirs, the ordering of the relative energies is not. For example if we use $Ti_4$ and $C_2$ clusters to define our atomic reservoirs, the energies per TiC pair of the four structures in Table 1 have the same ordering (the relative energies are $-2.58$, $-0.45$, $-0.21$ and 0.00 eV, respectively). Within the local-density (generalized-gradient) approximation to the DFT, the 32-unit rock-salt fragment and METCAR cluster are more stable than the metal-coated fullerene by 2.35 (2.56) and 1.10 (0.91) eV/pair, respectively. This result is in accord with the temperature dependence of the mass spectra observed by Tast et al. [5]. For low laser vaporization intensities and a relatively cold fullerene oven the mass spectra clearly shows a peak corresponding to the 62-metal-atom-coated fullerene. As the fullerene oven temperature increases, or the laser intensity is increased, the mass spectra shows the METCAR $C_{12}M_8$ peak increases. Since METCAR clusters are more stable, production of the metal-coated $C_{60}Ti_{62}$ clusters must be accomplished at low temperatures to prevent tunneling through or vibrating over transition states that would lead to destruction of the fullerene cage and subsequent production of the METCAR clusters. In principle production of rock-salt fragments should be the energetically most favorable outcome. This prediction is in accord with the bulk structure which is known to exhibit the rock-salt structure (see, e.g., Ref. [20]). However, significantly more energy is required to form this type of structure since all C–C bonds must be broken to assemble rock-salt fragments, suggesting a very large energy barrier to its formation starting from fullerenes.

Table 1
Comparson of relative stability, energy of HOMO level, and HOMO-LUMO gaps for different C/Ti clusters. Energies per pair of TiC atoms (EP) are measured with respect to the $C_4Ti_4$ rock-salt fragment. All energies are in eV. $Ti_b$ and $C_g$ designate bulk Ti and graphitic C atoms, respectively

| System | EP | HOMO | Gap |
|---|---|---|---|
| $C_{32}Ti_{32}$ | $-2.58$ | $-4.25$ | 0.50 |
| $C_{12}Ti_8 + 4Ti_b$ | $-1.48$ | $-2.76$ | 0.07 |
| $C_{60}Ti_{62} + 2C_g$ | $-0.23$ | $-3.21$ | 0.00 |
| $C_4Ti_4$ | 0.00 | $-4.53$ | 2.28 |

### 3.5. Vibrational properties

The lengthening of the C–C bonds in the fullerene cage when it is coated by the metal atoms should lead to softening of the C–C stretch modes. To address this point we have calculated the vibrational frequencies of the Raman-active $A_{1g}$ modes of the fullerene cage. Since the Ti atoms are four times heavier than the carbon atoms, modes involving Ti–C motion will couple only weakly to the modes involving C–C vibrations. Accordingly, we considered only the effects of carbon motion in calculating these frequencies. By diagonalizing a $(2 \times 2)$ $A_{1g}$ dynamical matrix we find pentagonal pinch and breathing modes with frequencies 1237 and 349 $cm^{-1}$, respectively. These modes are softer than the corresponding modes in the isolated fullerene which have frequencies 1470 and 496 $cm^{-1}$, respectively [21]. The electronic structure is only weakly perturbed by the breathing modes, but excitation of the pentagonal pinch mode leads to significant charge transfer between the $T_{2u}$ and $T_{1u}$ HOMO states.

Finally, we have performed calculations on $C_{60}V_{62}$, $C_{12}V_8$, $C_4V_4$, and $C_{32}V_{32}$ using Bachelet–

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[3] The ground state structure of the METCAR remains an active area of investigation. The point of importance for this Letter is whether a METCAR structure exists that is more stable than the $C_{60}Ti_{62}$ cluster. Our METCAR structure is characterized by a distortion of the $T_d$ symmetry. For a recent discussion on the present status of METCAR structures see Ref. [18].

[4] The cohesive energy for bulk Ti is 6.29 eV (LDA) and 5.09 eV (GGA); see Ref. [19].

Hamann–Schlüter pseudopotentials [22]. In accord with the above results we find the same ordering for the relative stabilities. The 32-unit rock-salt structure and the $C_{12}V_8$ METCAR cluster are more stable than $C_{60}V_{62}$ by approximately the same energies as shown in Table 1.

## 4. Summary

In summary, we have performed state-of-the-art calculations based on DFT and the generalized gradient approximation for several large clusters consisting of transition metal and carbon atoms. The $C_{60}M_{62}$ cluster is metastable with respect to METCAR clusters and rock-salt fragments. Experiments at higher temperature or higher laser fluence indeed suggest a higher proportion of METCAR clusters, whereas transformation of the metal-coated fullerene to the most stable rock-salt structure is apparently inhibited by a very large energy barrier. Dressing the fullerene cage with the sheath of transition metal atoms inhibits the C–C $\pi$ bonding which leads to a slightly larger cage consisting entirely of C–C $\sigma$ bonds. The $C_{60}M_{62}$ structure is stabilized by mixed ionic and covalent bonding between the 12 Ti atoms (situated above the C pentagons) and the fullerene, and the presence of a covalently bonded network of 50 Ti atoms that nicely fits around the Ti-decorated fullerene.

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## References

[1] A. Rosen, B. Wastberg, Z. Phys. D 12 (1989) 387.
[2] T. Guo et al., 257 (1992) 1661.
[3] K. Jackson, E. Kaxiras, M.R. Pederson, Phys. Rev. B 48 (1993) 17556.
[4] U. Zimmermann, N. Malinowski, U. Näher, S. Frank, T.P. Martin, Phys. Rev. Lett. 72 (1994) 3542.
[5] F. Tast, N. Malinowski, S. Frank, M. Heinebrodt, I.M.L. Billas, T.P. Martin, Phys. Rev. Lett. 77 (1996) 3529.
[6] F. Tast, N. Malinowski, S. Frank, M. Heinebrodt, I.M.L. Billas, T.P. Martin, Z. Phys. D 40 (1997) 351.
[7] M.R. Pederson, K.A. Jackson, Phys. Rev. B 41 (1990) 7453.
[8] K.A. Jackson, M.R. Pederson, Phys. Rev. B 42 (1991) 3276.
[9] A. Briley, M.R. Pederson, K.A. Jackson, D.C. Patton, D.V. Porezag, Phys. Rev. B 58 (1998) 1786.
[10] D.C. Patton, M.R. Pederson, D.V. Porezag, J. Kortus, unpublished.
[11] J.P. Perdew, Y. Wang, Phys. Rev. B 33 (1986) 8800.
[12] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[13] D.V. Porezag, Ph.D. Thesis, Technische Universität Chemnitz-Zwickau, 1997.
[14] M.R. Pederson, A.A. Quong, Phys. Rev. B 46 (1992) 13584.
[15] B.C. Guo, K.P. Kearns, A.W. Castleman, Science 255 (1992) 1412.
[16] B.V. Reddy, S.N. Khanna, P. Jena, Science 258 (1992) 1640.
[17] M. Methfessel, M. van Schilfgarde, M. Scheffler, Phys. Rev. Lett. 70 (1993) 29.
[18] S. Li, H. Wu, L.S. Wang, J. Am. Chem. Soc. 119 (1997) 7417.
[19] P.H.T. Phillipsen, E.J. Baerends, Phys. Rev. B 54 (1996) 5326.
[20] M. Sigalas, D.A. Papaconstantopoulos, N.C. Bacalis, Phys. Rev. B 45 (1992) 5777.
[21] A.A. Quong, M.R. Pederson, J.L. Feldman, Solid State Commun. 87 (1993) 535.
[22] G.B. Bachelet, D.R. Hamann, M. Schlüter, Phys. Rev. B 26 (1982) 4199.