Electronic Structure and Bonding in the Metallocarbohedrane Ti₈C₁₂

M. Methfessel, M. van Schilfgaarde, and M. Scheffler

(1) Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, Germany
(2) SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025

(Received 8 September 1992)

Total-energy and electronic-structure calculations are presented for a recently proposed dodecahedral cluster of eight titanium and twelve carbon atoms. The calculations were done using density-functional theory and a cluster full-potential linear muffin-tin orbital method which is suited to arbitrary geometries and permits direct evaluation of the forces. As in the C₆₀ molecule, the atoms form a spherical graphitelike shell with a threefold coordination at all sites. The calculated C-C and Ti-C bond lengths are 2.63 and 3.76 bohrs; the binding energy is 6.6 eV per atom. The bonding mechanism is quite different from that of the graphite crystal or the C₆₀ molecule.

PACS numbers: 36.40.+d, 31.20.Sy, 61.50.Lt

Since the first observation of the C₆₀ molecule [1], much effort has been invested in the study of this novel molecular cluster. In C₆₀, the carbon atoms form a hollow sphere consisting of fivefold and sixfold rings, whereby each atom has a coordination number of three. It can be considered a spherical form of graphite and it has been shown that the bonding mechanism is essentially the same. A short time ago, Guo, Kerns, and Castleman [2] discovered an unusually stable charged cluster with the stoichiometry Ti₈C₁₂. Furthermore, they were able to show that the eight Ti atoms are similarly coordinated. Later, analogous molecules with Hf, Zr, or V in place of Ti were identified [3, 4]. For neutral and ionized molecules of this type (named metallocarbohedrenes) they proposed the structure displayed in Fig. 1. The atoms are arranged at the corners of a dodecahedron with six C₂ dimers alternating with the eight Ti atoms. As in C₆₀, all atoms in this “soccerball-shaped” molecule are threefold coordinated; however, here only fivefold rings occur. Furthermore, the surface is more strongly curved and consequently the corresponding fullerene C₂₀ is not stable. Interestingly, Ti can form a metastable ω phase which has been interpreted as partly covalent [5].

The question thus arises whether the proposed structure is correct and, if yes, to what extent the bonding mechanism in this carbon-titanium molecule is analogous to that in the carbon fullerenes, as suggested in Ref. [2]. To shed light on this question, we have performed ab initio electronic structure calculations for Ti₈C₁₂ in the proposed geometry. The results confirm the structure, whereby the dodecahedron is deformed somewhat due to the different lengths of C-C and Ti-C bonds. By studying the electronic wave functions and the charge density, we have analyzed the bonding. We find that the electronic structure can be understood as C₂ molecular orbitals combining with the Ti d orbitals to make bonding cluster states. The Fermi energy lies between the bonding and nonbonding states, explaining the stability of the cluster. Contrary to previous expectations, no analog to the graphitic bonding in the C₆₀ molecule is found, showing that indeed Ti₈C₁₂ is a member of a new class of molecular clusters.

The calculations were done using a recently developed full-potential linear muffin-tin orbital (FP-LMTO) method which is designed for clusters, to be presented in detail elsewhere [6]. The basis for the representation of the electronic eigenstates consists of atom-centered spherical Hankel functions which are augmented by numerical solutions of the radial Schrödinger equation inside nonoverlapping atomic spheres. The combination of the augmentation technique with the use of LCAO-like atom-centered envelope functions leads to a very efficient basis set which can be applied to heavy and light elements equally well. As has been discussed previously [7], the main difficulty for a full-potential method using this basis set is to find a usable representation for the product of two such functions in the interstitial region (between the atomic spheres). As before, we represent these products as linear combinations of other atom-centered Hankel functions. In the new method, we first obtain an arbitrarily accurate representation for pairs of atoms.
arranged along the z axis. The expansion coefficients are tabulated as a function of the interatomic distance. For any other geometry, we obtain the needed expansion rapidly by evaluating the tabulated fit and applying rotation matrices. The electron-electron interaction is treated by the local-density approximation (LDA) [8,9] within density-functional theory; hereby the interstitial exchange-correlation quantities are obtained by numerical integration. In addition, it has been possible to derive an exact and practicable force theorem within this technique. In sum, the applied FP-LMTO method has these desirable features: (1) it can be applied to any cluster geometry (without the use of "empty spheres" or shape approximations to the density or potential); (2) it can be made arbitrarily accurate by increasing the precision of the initial pairwise fit; (3) the forces on the nuclei are available. Tests for typical molecules such as N2, CO2, H2O, H2S, and H2Se yield results in very good agreement with experiment (except for the typical overbinding due to the LDA) as well as previous state-of-the-art calculations where available.

In the present case, the muffin-tin radii were chosen 2.20 and 1.25 bohrs for Ti and C, respectively. LMTO's of kinetic energies −0.4, −1.0, and −2.0 Ry were used with angular momentum cutoffs of \( l_{\text{max}} = 2 \), 2, 1 on Ti and 2, 1, 1 on C, making a basis of 380 functions in total. The charge-density basis consisted of Hankel functions with kinetic energies −1, −3, −9, and −12 Ry with angular momentum cutoffs of \( l_{\text{max}} = 3 \), 6, 3, 1 on Ti and 3, 4, 3, 1 on C. Inside the spheres, the density and potential were expanded in spherical harmonics up to angular momentum \( l_{\text{max}} = 3 \). To speed up convergence, occupation numbers for the eigenstates were calculated using a Gaussian broadening of 0.02 Ry. With this broadening, we do not find any Jahn-Teller distortion [10]. It was found necessary to treat the high-lying Ti 3s and 3p levels with the same accuracy as the valence states by means of a "two-panel" technique.

The proposed dodecahedral structure can be viewed as a cube of Ti atoms, with one C2 dimer associated with each face. Symmetry operations are mirrors on the x-y, y-z, and z-x planes as well as the threefold rotations around the cube diagonals, generating a symmetry group of 24 elements. To calculate the equilibrium structure, the atoms were placed on the corners of an ideal dodecahedron with small random displacements to break the symmetry. While iterating to self-consistency, the atoms were moved to follow the forces until these were smaller than 0.01 Ry/bohr. In the relaxed structure, the symmetry is recovered and the C-C bond length has contracted to 2.63 bohrs while the Ti-C bond has expanded to 3.76 bohrs. The C and Ti atoms have almost the same distance from the cluster center, namely, 4.92 and 4.95 bohrs, respectively. We do not find the cubic geometry suggested in Ref. [11] on the basis of valence-bond arguments. The charge density for the valence states is displayed in Fig. 2. The calculated binding energy is 6.61 eV per atom, taking into account spin-polarization energies of 0.71 and 1.20 eV, respectively, for the free Ti and C atoms. For comparison, the binding energy per atom for crystalline TiC in the NaCl structure is only slightly larger at 7.16 eV (calculated using the technique of Ref. [7]), despite the twice as large coordination number. In summary, our calculation finds the distorted dodecahedral geometry stable and strongly bound for Ti5C12.

When Guo et al. proposed the dodecahedral structure for Ti5C12, they made the reasonable suggestion that the bonding mechanism is similar to that of graphite and C60. As first ingredient they postulated a network of Ti-C and C-C \( \sigma \) bonds, involving \( d-sp \) hybrids on the Ti atoms. Second, "\( \pi\) -bonding" states made from metal \( d_{\pi} \) and carbon \( p_{\pi} \) orbitals were assumed to take up the remaining electrons. The transition metal is assigned a relevant role in stabilizing the molecule by reducing the strain, due to the strong curvature, which would make a hypothetical \( C_{20} \) molecule unstable. This model would place sixty valence electrons into the \( \sigma \) bonding and twenty electrons into \( \pi \) bonding states.

Our calculations support a quite different view of the electronic structure. We find that a more appropriate description is that of well-defined C2 dimers whose orbitals bind with the nearest-neighbor Ti \( d \) orbitals. To support this view, Fig. 3 shows the density of states for Ti5C12. There are four well-separated "bands" below the Fermi energy \( E_{F} \). These correlate with the energy levels of the isolated C2 dimer (calculated at the same interatomic distance as in the cluster), also shown. A Mullikan projection onto the LMTO basis set was used to decompose the density of states into site and angular-momentum contributions [12]. The two lowest bands, containing six cluster states each, are mainly of C \( s \) character with a small amount of \( p \) character along the C-C bond mixed in. These are derived from the C2 bonding and antibonding \( \sigma \) states (1\( \sigma_{g} \) and 1\( \sigma_{u} \) in Fig. 3). The third
band (eighteen states) is in the same energy range as the
p-like bonding states in the dimer (1π\textsubscript{u} and 2σ\textsubscript{g} in Fig.
3). Finally, the band just below ε\textsubscript{p} (of which ten states
are occupied) can be associated with the two dimer antibo
dunding molecular orbitals, 1π\textsubscript{g}. The number of states
in each band is obtained correctly by multiplying the
dimer molecular orbital degeneracies with the number of
dimers in the cluster (six). This classification of the cluster
eigenstates is clearly visible in the partial charge den
sities and wave functions (Fig. 4). It is important that,
in the cluster, antibonding C\textsubscript{2} dimer states are occupied
which are unoccupied in the free dimer (fourth band).
This indicates a transfer of charge from the Ti to the
C atoms, in agreement with the electronegativities. The
four bands are of 90\%, 70\%, 70\%, and 40\% carbon char
acter, respectively. In total, we obtain valence charges of
4.36 on the carbon and 3.46 on the titanium atoms, i.e.,
a charge transfer of about 0.4 electron per atom. Our
calculated geometry and electronic structure agree well
with those of Ref. [13].

The bonding between carbon neighbors is due to the
first three bands. Bonding between Ti and C atoms has
some contributions from the second and third bands but
is mainly due to the fourth band. Figure 5 illustrates
how Ti-C bonding states can be made incorporating the
C\textsubscript{2} antibonding π states in a geometry with fivefold rings.
These states weaken the C-C bonds to some extent. The
unoccupied states above the Fermi energy are of practi
cally pure Ti character and would not contribute to the
bonding of the molecule if they were occupied. The en
ergy range of this nonbonding band overlaps slightly with
the fourth band. In total, there are 6 + 6 + 18 + 12 = 42
bonding states available in the first four bands. They
are filled almost completely by the eighty valence elec
trons. Since the Fermi level falls between the bond-

FIG. 3. Density of states for the Ti\textsubscript{6}C\textsubscript{12} molecule. Eigen
values were broadened by Gaussians of width 0.01 Ry. The energy levels of the nonmagnetic free C and Ti atoms and of the C\textsubscript{2} dimer (with the same distance as in Ti\textsubscript{6}C\textsubscript{12}) are also shown.

FIG. 4. Plots in a pentagonal face of a typical wave function (left) and the summed electron density (right) for each of the four occupied bands. For the third band, the shown wave function is of 1π\textsubscript{u} character on the C\textsubscript{2} dimer; others of 2σ\textsubscript{g} character exist in the same band. Shown are the intersti
tial functions extended smoothly into the muffin-tin spheres.
First contour and contour spacing are 0 and 10 for wave func
tions and 2.5 and 5.0 for densities in units of 10\textsuperscript{-3} bohr\textsuperscript{-3}. Negative contours are dashed; contour for zero is dotted.

ing and nonbonding states, the cluster is exceptionally
strongly bound. We conclude that a similar cluster with a
considerably earlier or later transition metal in place of
Ti would be less stable. Interesting possibilities, how
ever, open up if, in addition, some C atoms are replaced
by neighbors in the periodic table, keeping the total num
ber of valence electrons close to eighty. The isoelectron
ic metals Zr and Hf are of course obvious candidates for
a stable cluster of the same type as Ti\textsubscript{6}C\textsubscript{12}, which ind
eed have been found recently [3]. For V\textsubscript{6}C\textsubscript{12}, the Fermi
energy will be shifted upward but should still lie in the
valley of the density of states.

All cluster eigenstates have definite σ or π character.
FIG. 5. Sketch of the way in which the Ti d orbitals combine with the C₂ dimer antibonding $p_\pi$ wave functions to make bonding cluster wave functions. The carbon atom at the top is a member of another C₂ dimer not in the plane of the paper.

along the C-C bond. Is it possible to classify the Ti-C bonds in the same way? The Ti d orbitals which could participate hereby must be compatible with the C₃v point symmetry at a Ti site. The arrangement of the three C neighbors is essentially a tetrahedral coordination with a missing fourth corner atom. For this symmetry it is possible to define combinations of the d orbitals which are directed along the nearest-neighbor bonds. However, inspection of the forty occupied eigenstates did not yield a generally valid picture of well-defined Ti-C $\sigma$ bonding.

To understand this, it is important to realize that the C₂ dimer forms a very strong unit in the cluster. The C₂ molecular orbitals, which force their shape onto the cluster wave functions, are at unusual angles relative to the Ti-C bond. An essential ingredient to the binding is the flexibility of the d orbitals which makes it possible to "hook together" these functions into bonding cluster states. Of the total valence charge on the Ti atoms, only 4.5% and 3.9% is associated with the s and p orbitals, respectively. Thus, it is essentially only the Ti d orbitals which participate in the bonding with carbon.

Nevertheless, it might be tempting to try to reinterpret our picture of the bonding as a graphitelike mechanism. This could be fueled by the fact that the number of states in the three lower bands (thirty) equals the number of possible bonding combinations of the $sp^2$-like orbitals from twenty atoms. However, this approach does not seem useful. Bonding in a graphite layer is understood to be due to two main contributions: (1) $\sigma$ bonding of localized and strongly directed $sp^2$ orbitals which point to the three neighbors; (2) additional $\pi$ bonding due to the $p_z$ orbitals perpendicular to the plane. Neither of these two mechanisms can be identified in our calculated results. We conclude that the bond of a Ti atom to its three carbon neighbors is clearly distinct from the bonding in graphite. This is confirmed by the existence of multicage structures such as Zr₂C₁₄ [14] for which no fullerene analogies exist. These structures are possible because the flexibility of the metal d orbitals is sufficient to hook together four dimers instead of three. The fact that Ti₈C₁₂ can bond to eight ammonia molecules was explained in a similar way [3].

In summary, our $ab$ initio DFT-LDA calculation for the Ti₈C₁₂ molecule in the dodecahedral structure obtains a stable and strongly bound geometry. The dodecahedron is distorted somewhat because the C-C bonds are shorter compared to the Ti-C interatomic distance. The electronic structure can be understood as well-defined C₂ dimers whose molecular orbitals combine with the Ti d functions to make bonding cluster wave functions. The Ti-C bonding is largely due to those cluster wave functions which are derived from the dimer antibonding $p_\pi$ combinations and which are unoccupied in the free C₂ dimer. The Fermi energy lies between the bonding states and nonbonding Ti states, explaining the stability of the cluster. Overall, we find no significant similarity to the bonding mechanism which stabilizes graphite and the C₆₀ molecule.

M.v.S. was supported by ONR Contract No. N00014-89-0132.

(a) Permanent address: Institut für Halbleiterphysik, Walter-Korsing-Strasse 2, O-1200 Frankfurt/Oder, Germany.
[12] V. Fiorentini, M. Methfessel, and M. Scheffler (to be published). Note that the decomposition projects onto the atom-centered basis functions and not onto the angular momenta inside the spheres; thus the partial charges depend only weakly on the sphere radii and there is no separate interstitial contribution. Angular momenta are relative to local coordinate systems on the Ti and C atoms with the z axis pointing out of the cluster.