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Phase stabilities and structural relaxations in substoichiometric TiC_{1-x}

Håkan W. Hugosson,[1] Pavel Korzhavyi,[2] Ulf Jansson,[3] Börje Johansson,[1,2] and Olle Eriksson[1]
[1] *Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden*
[2] *Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology, S-100 44 Stockholm, Sweden*
[3] *Inorganic Chemistry Group, Ångström Laboratory, Uppsala University, Box 538, S-751 21 Uppsala, Sweden*

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First-principles calculations have been used to study the effect of vacancies and relaxation around the vacancy sites in substoichiometric TiC_{1-x}. The effect of relaxation on phase stabilities, equilibrium volumes, and electronic structure of the substoichiometric phases was studied using a combined approach of pseudopotential plane wave and full-potential linear muffin-tin orbital methods. A relaxation away from the vacancies was found for the titanium atoms, the magnitude of which increased with vacancy concentration and the inclusion of nearest-neighbor carbon atom relaxation. The inclusion of local relaxations was found to correctly predict the off-stoichiometric equilibrium composition of titanium carbide. The anomalous volume behavior of TiC at small vacancy concentration is explained as an effect of the local relaxation of the atoms surrounding the vacancy sites, but we do not find that the lattice parameter of any of the studied stoichiometries is larger than that of ideal stoichiometric TiC.

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I. INTRODUCTION

The transition metal carbides have a unique combination of properties, e.g., high hardness, high melting point, excellent electrical conductivity, and, in some cases, superconductivity, making them suitable as bulk or thin film materials in many technological applications, for example, as coatings on cutting tools. This combination of attractive properties has also attracted a large number of experimental and theoretical investigations. Cubic TiC, which is the subject of study here, is an important thin-film material used in coating layers and in binderless cemented carbides together with WC and as a component material in high-speed steels. The cubic NaCl phase of TiC displays deviations in stoichiometry over a wide range of homogeneity, from $TiC_{0.50}$ to $TiC_{0.97}$, this being caused by vacancies in the carbon sublattice. The vacancies have unusual effects on the physical properties of TiC, the most conspicuous effect being that the lattice constant appears to be almost constant or increasing for small vacancy concentrations.[1] Experimentally the lattice parameter for TiC_x expands for $1.0>x>0.9$ and shrinks for $0.9>x>0.5$, the total change in lattice parameter being less than 1%.

Given the technological interest in transition metal carbides and the large experimental activity, many theoretical calculations have been made on these systems using a wide variety of techniques. The latest comprehensive reviews, to our knowledge, of the field are due to Schwarz[2] and Johansson.[3] Substoichiometric transition metal carbide/nitride compounds have been studied, for example, by Ivanovskii and coworkers using a Green's function linear muffin-tin orbital (LMTO) method[4] and the enthalpies of formation and effective cluster interactions of substoichiometric VC_{1-x} have been studied by Ozolins and Häglund using a full-potential LMTO method.[5] The effect of vacancies on the relative phase stabilities of several substoichiometric MoC_{1-x} phases was studied in a previous work by Hugosson and co-workers.[6] The effect of vacancies on TiC has been studied in previous theoretical works. Redinger and coworkers studied substoichiometric $TiC_{0.75}$ using a self-consistent augmented plane wave (APW) method and a model structure with ordered vacancies not allowing for local relaxations around the vacancies.[7] A recent investigation of $TiC_{1-x}N_x$ by Jhi and co-workers reported on a mechanism coupling the shear modulus of TiC with the valence electron concen-tration.[8] Relaxations around vacancies in substoichiometric TiC_{1-x} and TiN_{1-x} studied using complete neglect of differential overlap/2 cluster calculations were performed by Capkova and Skala.[9] More recently Tan *et al.* also studied TiC_x, $x=1.00$–0.50, using a tight-binding model that allowed for structural relaxations around the vacancy sites, in which a small increase of the lattice parameter was found for small vacancy concentrations.[10] The effect of local relaxations around vacancies has been studied for pure transition metals by Meyer and Fähnle using a pseudopotential method[11] and by Söderlind *et al.* using a combined approach with full potential-LMTO and pseudopotentials.[12]

The concentration of vacancies in pure metals is usually less than one percent even at pre-melting temperatures. In contrast, up to one-half of the carbon lattice sites may be vacant in TiC_{1-x}, thus a larger number of vacancies and the effects of their relative positions need to be taken into account in studies of such compounds. The aim of the work presented here is to investigate the effect of vacancies over a large range of stoichiometry in substoichiometric titanium carbide using a full-potential all-electron method and accounting for the effect of relaxation around the vacancy sites by making a detailed analysis of the changes in geometric structure, phase stabilities, and electronic structure. Such a detailed all-electron study on the effect of vacancies and relaxation over a large range of stoichiometry has never before been done for compounds and, in this particular case, not for the transition metal carbides.

II. THEORETICAL METHOD

The calculations presented here have been made using a full-potential linear muffin-tin orbital method (FP-LMTO)

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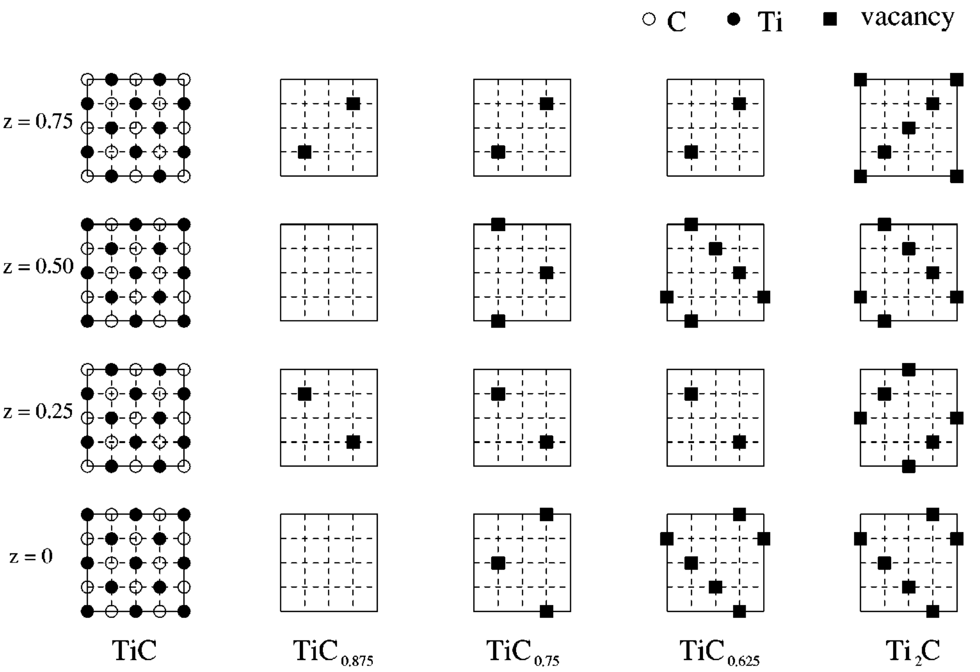

FIG. 1. Structures of the stoichiometric and substoichiometric TiC phases studied using a 16-atom supercell. Four planes of the crystal are shown from top to bottom, z designating the different planes of the crystal. In the leftmost figure, the carbon atoms (unfilled circles) and the titanium atoms (filled circles) are shown while in the following figures only the position of the vacancies (filled squares), on the same lattice, are shown.

within the local density approximation (LDA) of density functional theory.[13,14] The function used for the exchange-correlation has been the Hedin-Lundqvist parametrization.[15] In the FP-LMTO method the unit cell is divided into nonoverlapping muffin-tin spheres, inside of which the basis functions are expanded in spherical harmonics up to a cutoff in angular momentum, $l_{max}=6$. The basis functions in the interstitial region, outside the muffin-tin spheres, are Neumann or Hankel functions. To speed up the convergence, each eigenvalue was convoluted with a Gaussian of a width of 20 mRy.[16] Energy convergence in terms of the number of k points has also been reached, 27–39 k points, depending on setup, in the irreducible part of the Brillouin zone has been used. When describing the atoms of the crystal, the electronic states are divided into core, pseudocore, and valence states. For the titanium atom the $5s$ and $4d$ electronic states were treated as valence states while the $4p$ and $4s$ electronic states were treated as pseudocore. For the carbon atom the $1s$ levels were treated as core electronic states while the $2s$ and $2p$ were treated as valence electron states. The pseudocore and valence states were allowed to hybridize in one common energy panel.

Substoichiometric titanium carbide was studied from stoichiometric TiC down to $\text{TiC}_{0.25}$, using four supercell setups; with 4, 8, 16, and 32 atoms, respectively. Relaxation of the structures was made in three steps, first the NaCl structure was relaxed in the lattice parameter a for the different stoichiometries. Local relaxations around the vacancy sites were then studied by first applying forces to the unrelaxed structure (at a lattice parameter close to the equilibrium). The relaxations have been performed using the *ab initio* total energy and molecular dynamics program VASP.[17] The locally relaxed equilibrium structure found using the pseudopotential method was then transfered into the FP-LMTO method to find the equilibrium lattice constant and ground-state energy for the relaxed structure.[18] The combination of these two methods, full-potential and psuedopotential plane wave, was made in order to combine the efficient implementation of forces in the pseudopotential plane wave method with the high accuracy in total energy of the full-potential method. A total of 21 phases and structures were studied and for each phase and structure, relaxed and unrelaxed, the energy was calculated at 6–8 different volumes in order to find the equilibrium volume and total energy. The total energy vs volume curves were fitted to a Murnaghan equation of state to find theoretical ground state energies and equilibrium volumes. The bulk moduli have likewise been obtained from the Murnaghan equation.

III. UNRELAXED TiC_{1-x} STRUCTURES

In order to study the cubic phase for several stoichiometries, from $\text{TiC}_{1.00}$ to $\text{TiC}_{0.50}$ (Ti_2C), a supercell with an fcc lattice and a basis with 8 titanium atoms and 8 carbon atoms was created. The carbon atoms were subsequently removed creating $\text{TiC}_{0.875}$, $\text{TiC}_{0.75}$, $\text{TiC}_{0.625}$, and finally Ti_2C. These structures are shown in Figs. 1–3. Here one can clearly see the structures of the vacancies formed for every stoichiometry. By the gradual removal of C atoms the stoichiometric Ti_2C phase with ‘‘striped’’ vacancy structures reported in Ref. 19 is reached. The energy of formation being defined as

$$E_{\text{form}}=\frac{E(\text{Ti}_m\text{C}_n)-mE(\text{Ti}_{hcp})-nE(\text{C}_{graphite})}{n+m}, \tag{1}$$

where n and m are the number of nonmetal and metal atoms used in the super cell, was calculated for the structures and stoichiometries studied. The energies of formation and equilibrium volumes as a function of carbon content for all the unrelaxed (and relaxed) phases studied are shown in Fig. 4 and Fig. 5 and are collected in Table I. From the figures we can see that the substoichiometric TiC_{1-x} phases, from 50%

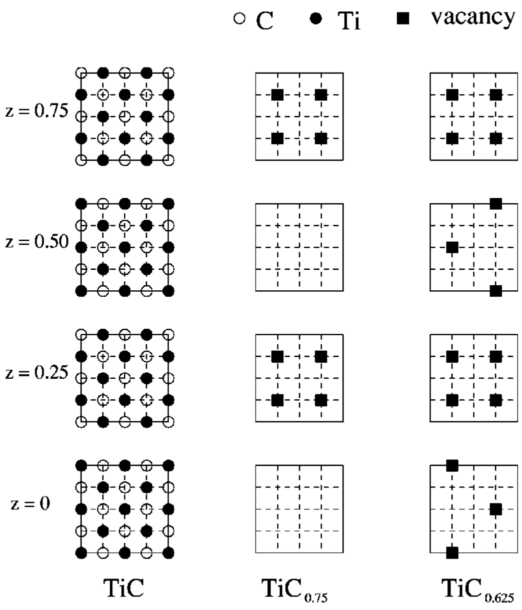

FIG. 2. Structures of the second choice using a 16-atom supercell studied for substoichiometric TiC$_{0.75}$ and TiC$_{0.625}$. The key to the figures is as in Fig. 1.

to 33% carbon content, are all less stable than the stoichiometric TiC but more stable than TiC plus hcp Ti, at their respective carbon contents. This indicates that the substoichiometric TiC$_{1-x}$ phases are all stable down to 33% carbon content that is consistent with the wide homogeneity range of TiC$_{1-x}$, as known from the experimental phase diagram.

Since there are several combinations of vacancies possible, the choice of vacancy positions has been made in order to reach the Ti$_2$C structure with ''stripes'' of vacancies. For TiC$_{0.75}$ and TiC$_{0.625}$ another choice of vacancy positions has also been studied, hereafter reffered to as the ''second choice'' and is shown in Fig. 2. It is seen that the choice of vacancy positions greatly affects the energy of formation and that the second choices are less favorable in energy than the first. This can be understood since in the case of TiC$_{0.75}$ the first choice, shown in Fig. 1, there are two types of Ti atoms; one with 1 vacancy nearest neighbor (VNN) and the other with 2 VNN's. The second choice, shown in Fig. 2, removes all the vacancies in one of the repeating layers and none in the second, creating a larger number of Ti atoms with 2 VNN's and other Ti atoms with 0 VNN's. The same reasoning in the case of TiC$_{0.625}$ shows that here also a larger number of Ti atoms with many vacancy nearest-neighbors are created compared to the first choice. Thus the more even distribution of VNN's is seen to be the energetically most favorable in both cases.

A larger supercell containing 32 atoms was also studied with zero and one carbon vacancy, forming TiC$_{0.9375}$, since this structure can allow for relaxations also of the nearest-neighbor carbon atoms, which will be discussed more in a section below. The energies of formation found for this setup (see Fig. 4) are in good agreement with those from the 16-atom supercell showing that convergence has been reached in terms of supercell size and choice of vacancy positions.

A smaller supercell with a simple cubic lattice and a basis containing 4 Ti and 4 C was used so that a comparison of the results could be made to determine the effect of supercell size and ordering of vacancies. The setup for the smaller supercell is shown in Fig. 3 and it is seen that the TiC$_{0.75}$ setup using this supercell is the same as the ''second choice'' of vacancy positions using the 16-atom supercell, and the energy of these two is also seen to be the same. The 8-atom supercell at TiC$_{0.50}$ is seen to be very much less favorable than the TiC$_{0.50}$ using the 16-atom supercell and once again this can be understood since the 8-atom supercell creates a number of Ti atoms that have no less than four vacancy nearest neighbors. From this study of the smaller supercell a

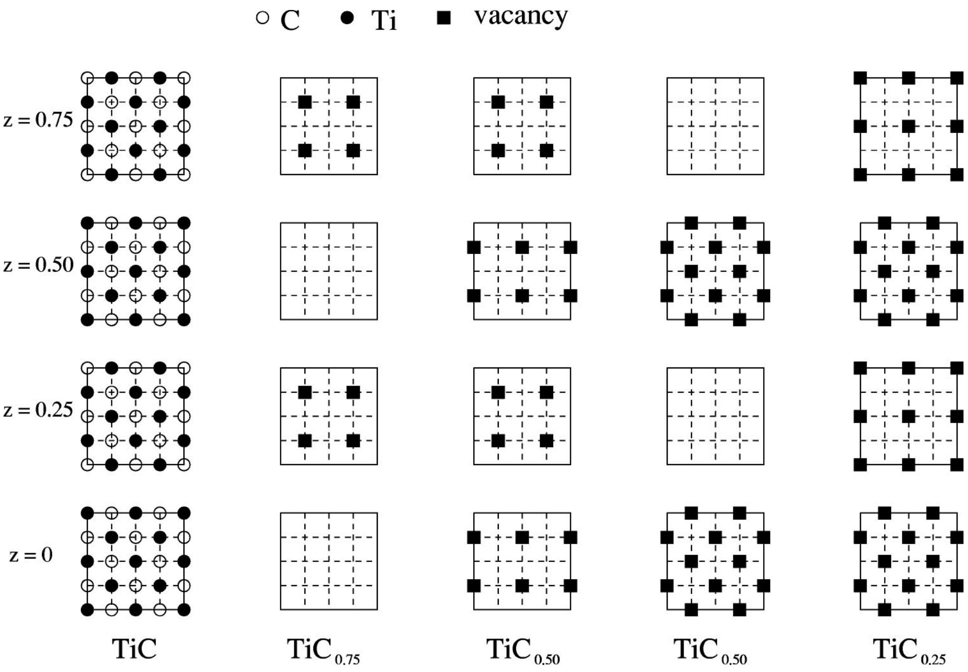

FIG. 3. The structures studied with the eight-atom supercell. The key to the figures is as in Fig. 1.

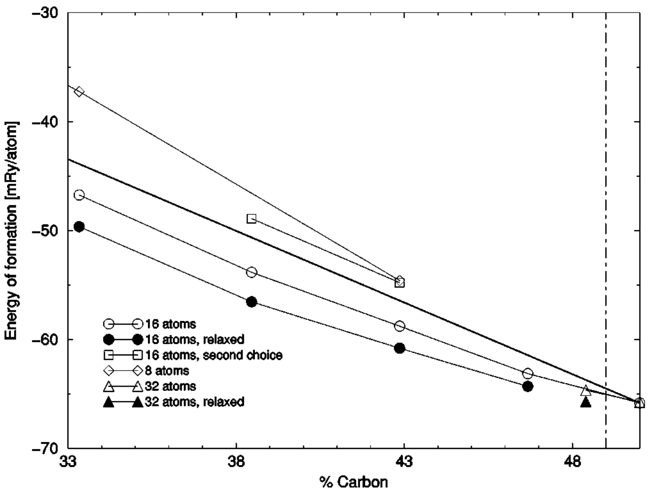

FIG. 4. The energies of formation for the stoichiometries studied as a function of carbon content. The results using different vacancy positions and supercells are shown and the energy of stoichiometric TiC plus hcp Ti is indicated by a solid line. The equilibrium carbon content of substoichiometric titanium carbide being $TiC_{0.97}$ is indicated by a dashed-dotted line.

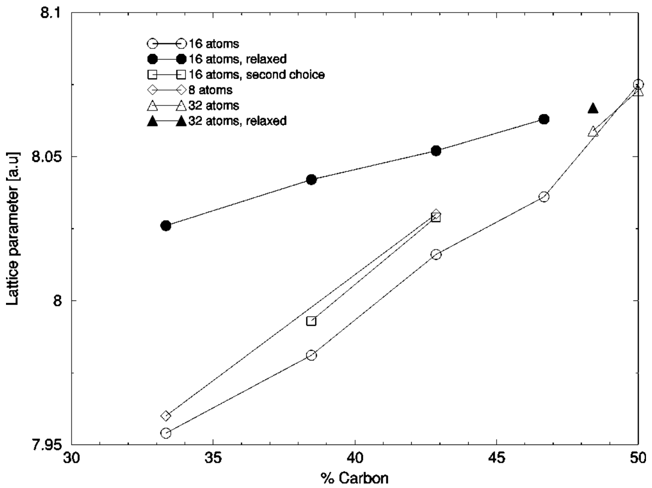

FIG. 5. The equilibrium lattice parameters for the stoichiometries studied as a function of carbon content. The results using different vacancy positions and supercells are also shown.

qualitatively different picture of the effect of vacancies on the structure is observed, even indicating that the substoichiometric TiC_{1-x} would not be stable, something that is shown to be incorrect from the study using the larger supercells. A second smaller setup using 4 atoms was also constructed in order to calculate the energy of the $L11$ structure. The total energies and volumes were found to be consistent with those from the other setups.

In total the effect of positions of vacancies is seen to be very important, even to the extent that using a too small supercell misses important physical properties like overall stability of the compounds. The structures resulting in Ti atoms with a larger number of vacancy nearest neighbors than the average is less energetically favorable than those with a more even distribution of vacancy neighbors.

IV. RELAXED TiC_{1-x} STRUCTURES

The 16-atom supercells allow for relaxation of the nearest-neighbor Ti atoms around the vacancy but not for the second coordination shell of carbon atoms. For the structure with one vacancy ($TiC_{0.875}$) where the movement of the atoms is the simplest, it is found that theoretically the Ti atoms relax away from the carbon vacancy by 0.049 Å. This is illustrated in Fig. 6 and is in accordance with experiment where an outward relaxation is also found. Experiments by diffuse-neutron scattering on $TiC_{0.76}$ have found the relaxation of the titanium atoms to be 0.03 Å (Ref. 20) while a study using x-ray diffraction measurements on $TiC_{0.94}$ found it to be 0.097 Å.[21] A supercell with 15 carbon atoms and 16 titanium atoms has also been studied and relaxed. This setup allows for relaxation of both nearest-neighbor titanium atoms and next-nearest-neighbor carbon atoms and showed that the outward relaxation of the titanium atoms increased to 0.069 Å and that the carbon atoms relaxed inward, towards the vacancies, by 0.026 Å. This shows that the inward relaxation of the carbon atoms allows for a greater outward relaxation of the titanium atoms.

The relaxation of the titanium atoms is always outward, away from the neighboring vacancies, irrespective of carbon content. The relaxation distance as a function of carbon content is shown in Fig. 7. The magnitude of the outward relaxation is strongly dependent on the stoichiometry, i.e., the

TABLE I. Number of atoms used in the supercell, if the supercell was relaxed or not, equilibrium lattice parameters a_{eq} (a.u.) and energies of formation E_{form} (mRy/atom) for the TiC_{1-x} phases studied. Please note that two choices of vacancy positions have been studied for some phases, indicated by a (2) for the second choice.

Phase	No. of atoms	Relax	a_{eq} (a.u.)	E_{form}
TiC	2	no	8.07	−65.8
TiC	4	no	8.07	−65.8
TiC	16	no	8.07	−65.8
TiC	32	no	8.07	−65.7
$TiC_{0.9375}$	31	no	8.06	−64.7
$TiC_{0.9375}$	31	yes	8.07	−65.7
$TiC_{0.875}$	15	no	8.07	−63.1
$TiC_{0.875}$	15	yes	8.04	−64.3
$TiC_{0.75}$	14	no	8.02	−58.8
$TiC_{0.75}$	14	yes	8.05	−60.8
$TiC_{0.75}$ (2)	14	no	8.03	−54.8
$TiC_{0.75}$	7	no	8.03	−54.6
$TiC_{0.625}$	13	no	7.99	−53.8
$TiC_{0.625}$	13	yes	8.01	−56.6
$TiC_{0.625}$ (2)	13	no	7.98	−48.9
$TiC_{0.625}$ (2)	13	yes	8.04	−49.8
$TiC_{0.50}$	12	no	7.95	−46.7
$TiC_{0.50}$	12	yes	8.03	−49.7
$TiC_{0.50}$	6	no	7.96	−37.2
$TiC_{0.50}$ ($L11$)	3	no	7.93	−49.1
$TiC_{0.25}$	5	no	7.85	−15.7

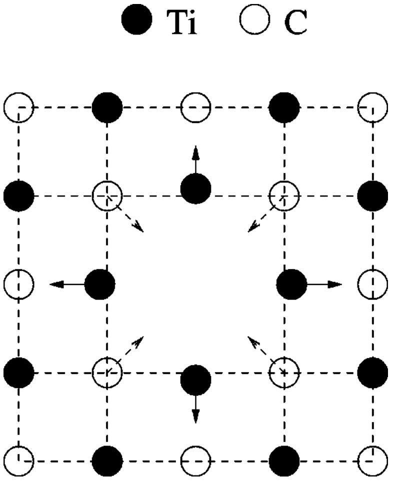

FIG. 6. The solid arrows indicate schematically the relaxation of the titanium atoms in a structure with one vacancy, shown in the [100] plane of the crystal. If next-nearest neighbor relaxations are also included the C atoms will relax inwards towards the vacancy, indicated by dashed arrows. When studying more substoichiometric structures the relaxation was also always found to be outward, away from the vacancy.

more vacancy neighbors a titanium atom has, the larger the relaxation is towards the remaining carbon atoms. The relaxation distance in the Ti_2C is the largest of the phases studied, because every titanium atoms has only three nearest-neighbor carbon atoms.

Previous theoretical works have given other results for the relaxation. Cluster calculations[9] have found the outward relaxation to be 0.107 Å and tight binding methods[10] determined it to be around 0.1 Å. Like in our study using a 32-atom supercell, the tight binding work using a 64-atom supercell also showed an inward relaxation of the nearest-neighbor carbon atoms. The outward relaxation of the titanium atoms can be understood since the bonding in these transition metal carbides is dominated by the strong directional *p-d* bonds between the carbon and titanium atoms. The titanium atoms that lose one of their nearest-neighbor carbon atoms are drawn away from the vacancy by the remaining *p-d* bonds that are strengthened. This is in contrast to the relaxation in pure transition metals were the atoms relax inward, towards the vacancy,[12] showing the difference to the metallic bonding with its more homogeneous distribution of charge.

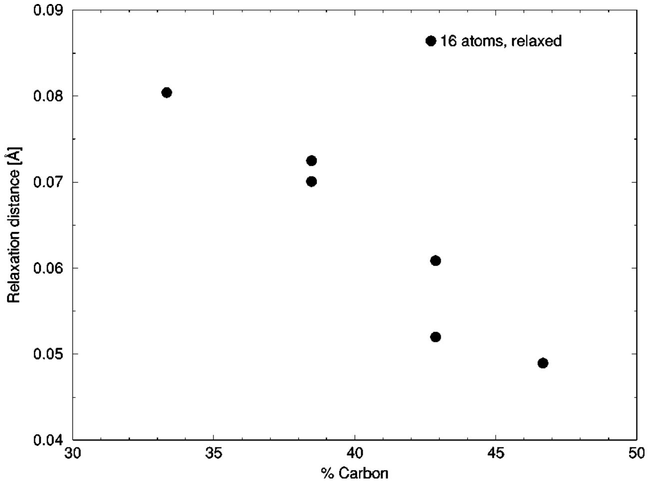

FIG. 7. The relaxation distance of titanium atoms as a function of carbon content. Note that there are two structures with different vacancy positions at some stoichiometries resulting in different magnitudes of relaxation.

From Fig. 4, Fig. 5, and Table I one can primarily conclude that the effect of the local relaxations of the atoms around the vacancy is a lowering of the formation energies by something of the order of 1–3 mRy per atom. The effect of local relaxations around the vacancy, as opposed to the total relaxation of the whole lattice, has also been studied in the previous work by Tan and co-workers using a tight binding method.[10] In their study the total effect of relaxing the Ti atoms was an increase of the lattice parameter for small vacancy concentrations. Our theoretical lattice parameters agree with experiment to within the usual LDA overestimation of the bonding, with the theoretical values being 1–2 % less than those found experimentally. The effect of the local relaxations on the equilibrium volume is seen, in Fig 5, to be an increase of the lattice parameter, though not large enough to result in a lattice parameter larger than that of stoichiometric TiC. The previous theoretical study by Tan and co-workers found a small expansion or contraction of the lattice parameter, depending on choice of vacancy positions, for small vacancy concentrations. In our study we only find a contraction, this can be attributed to the fact that the outward relaxation of the titanium atoms is smaller in our study, as discussed above. This in turn may be due to the smaller supercell used in this study; 32 atoms compared to 64.

The effect of the magnitude of the outward relaxation of the Ti atoms on the equilibrium lattice parameter was also studied. The theoretical equilibrium lattice parameter was calculated for substoichiometric $TiC_{0.875}$ using three magnitudes of outward relaxation. First a relaxation of 0.030 Å (from the diffuse-neutron scattering experiments[20]), then the theoretically relaxed value of 0.049 Å and last the experimental value from the x-ray diffraction measurements of 0.100 Å (Ref. 21) were used. We found that the theoretical equilibrium lattice parameter increased with increasing Ti relaxation distance. The equilibrium lattice parameter was also larger than the lattice parameter of stoichiometric TiC for the study using a relaxation distance of 0.100 Å. This indicates that there is a threshold for the Ti relaxation distance above which the lattice parameter for substoichiometric TiC_{1-x} is greater than that of stoichiometric TiC.

The magnitude of the local relaxation depends on the vacancy concentration and supercell size used; the larger the supercell the more of the relaxation is local around a vacancy, and the less is the overall relaxation of the lattice. The effect of the local relaxation on the lattice parameter is also seen to be larger for the more substoichiometric structures, resulting in a ‘‘flattening’’ of the lattice parameter versus carbon content curve. One can note that the total change, when going from TiC to Ti_2C, in lattice parameter for the relaxed structures is very close to that found experimentally, the change being around 1%.

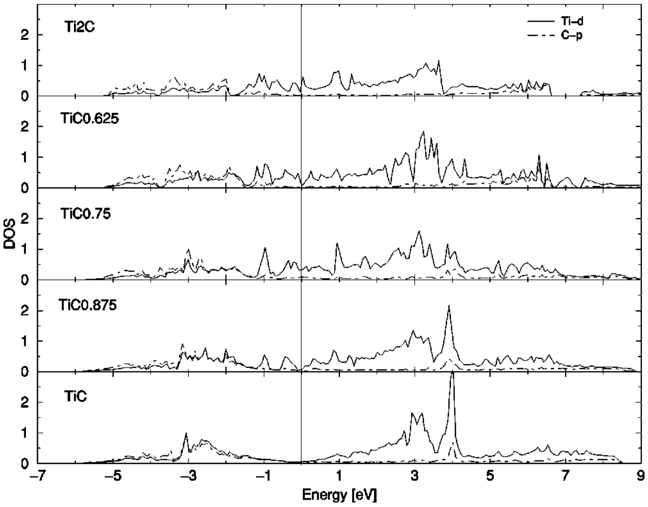

FIG. 8. Partial density of states for the unrelaxed TiC-Ti_2C phases. The Fermi level is indicated by a solid line.

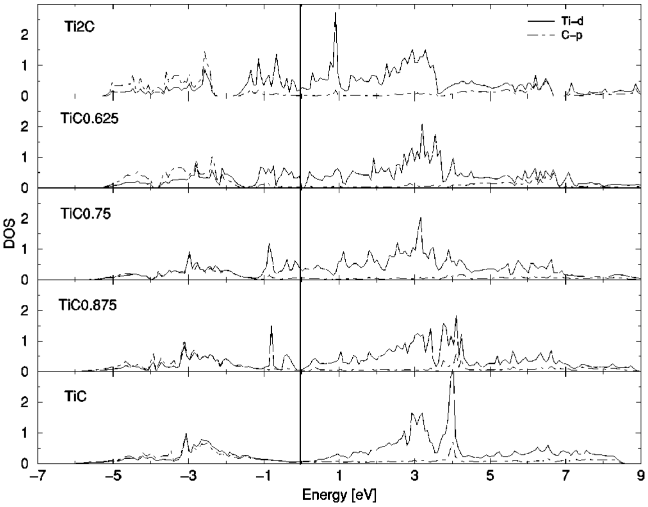

FIG. 9. Partial density of states for the relaxed TiC-Ti_2C phases. The Fermi level is indicated by a solid line.

Comparing the effect of relaxation on the different choices of vacancy positions, the ‘‘second choice’’ for the two vacancies in $TiC_{0.75}$ is clearly less favorable since the titanium atom with two vacancies on opposite sides does not allow relaxation in any direction, and it is also found that there is no relaxation in this structure. When discussing the influence of the smaller supercells, one can thus conclude that the largest approximation when studying substoichiometric compounds with a small supercell is not that one excludes the effect of relaxation around the atoms (often not possible for reasons of symmetry) but rather that one is more limited in the choice of positions of vacancies.

The effect of local relaxations is also necessary in order to explain that TiC is experimentally never found to be fully stoichiometric (as seen from its phase diagram). The unrelaxed energy of formation curves does not have a minimum at any $x \neq 1.00$. After relaxation the minimum in the energy of formation as a function of carbon content is seen to be situated, since the energies of formation for TiC and $TiC_{0.9375}$ are almost equal, not at the stoichiometric TiC but at a small concentration of vacancies between $x=0.94$ and $x=1.00$. This is important since it means that the formation of vacancies is energetically favorable even at zero temperature. When carbon atoms are removed the number of carbon-titanium bonds is reduced, causing an increase in energy as seen in the unrelaxed energies of formation. Since the energy of formation for the unrelaxed structures does not display a minimum at low-vacancy concentrations, we see that the formation of vacancies is made favorable by a strengthening of the remaining bonds after relaxation of the titanium atom positions. This is also indicated in the changes in the electronic structure, discussed below.

A. Electronic structure

The partial density of states for the unrelaxed structure, over a range of vacancy concentrations, is shown in Fig. 8. The bottom picture shows stoichiometric TiC and the top picture displays the Ti_2C structure. The effect on the electronic structure of transition metal carbides by the inclusion of vacancies has already been more closely examined in an earlier work.[6] The TiC density of states (DOS) shows two main regions where the first region is a highly bonding part from -5 eV to the Fermi level containing strongly hybridized C *p* and Ti *d* states followed by a second region of Ti *d* states representing Ti-Ti bonds. When vacancies are included certain vacancy related structures are seen to emerge below and around the Fermi level, called *vacancy peaks*. These vacancy peaks are of mainly Ti *d* character and very localized. The DOS is then gradually changed until the DOS for the Ti_2C is reached where there is a separation between the hybridizing C *p* Ti *d* part of the DOS and the Ti *d* part.

The effect of relaxation on the electronic structure is shown in Fig. 9 and the main difference is that the hybridizing C *p* Ti *d* part of the DOS is lowered in energy, an effect that is best illustrated by an inspection of the Ti_2C DOS. This lowering in energy can be understood since the effect of the local relaxation is a decrease of the distance between the remaining Ti and C atoms that results in a greater overlap between the electronic orbitals. A general sharpening of the vacancy peaks can also be seen when relaxations are included indicating a larger localization.

V. BULK MODULI

Hardness is one of the most technologically significant properties of the transition metal carbides. Hardness is determined by the creation and movement of dislocations and can therefore be considered to be controlled by two factors; the first is the energy needed to create the dislocations and the second how these dislocations are able to move in the system. The hardness of a material is thus not entirely given by the electronic structure but the first factor, the energy of creation of dislocations, can be modeled theoretically by calcu-

TABLE II. Bulk modulus for some of the substoichiometric titanium carbide phases studied.

Phase	No. of atoms	Relaxed	Bulk modulus (GPa)
TiC	16	no	278
$TiC_{0.875}$	15	no	247
$TiC_{0.875}$	15	yes	262
$TiC_{0.75}$	14	no	243
$TiC_{0.75}$	14	yes	243
$TiC_{0.625}$	13	no	228
$TiC_{0.625}$	13	yes	226
$TiC_{0.50}$	12	no	213
$TiC_{0.50}$	12	yes	204

lating the bulk modulus and/or the shear modulus of the material. The bulk modulus is an isotropic compression of the lattice and is easily accessible from the theoretical total energy versus volume curves necessary for determination of the equilibrium volumes and energies while a distortion of the lattice is necessary to calculate the shear modulus. We thus caution the reader that the bulk modulus that is often regarded as a measure of hardness does not contain the full information on material hardness. However, a plot of hardness versus e.g., bulk modulus for some of the technologically most interesting materials (BN, diamond, RuO_2) shows a linear relationship.[22] Having said this, we list and display the calculated bulk moduli for the different TiC stoichiometries in Table II and Fig. 10.

The bulk modulus decreases when introducing vacancies into stoichiometric titanium carbide and this can be understood since the bonding energy in the system is decreased. The experimentally reported value for the bulk modulus is 242 GPa for $TiC_{0.91}$.[23] Generally the bulk modulus of the relaxed structures is lower than that of the unrelaxed, this being due to the increase in lattice parameter from the relaxation. However, it is seen that the bulk modulus for the relaxed structure with one vacancy is larger than that of the unrelaxed structure, this is due to the lowering of the energy (strengthening of the bonds) from the relaxation coupled to a smaller expansion of the lattice.

VI. CONCLUSIONS

We have performed studies of substoichiometric TiC_{1-x} for a wide range of vacancy concentrations using an accurate all-electron full-potential method. The structures were relaxed using a plane-wave pseudopotential method, after which the relaxed structures were exported to the full-potential method. In this work we studied the effect of the positions of the vacancies and also allowed for local relaxations of the atoms around the vacancies. Such a detailed all-electron study on the effect of vacancies and relaxation over a large range of stoichiometry has never before been done for substoichiometric compounds. The results can be summarized in the following points.

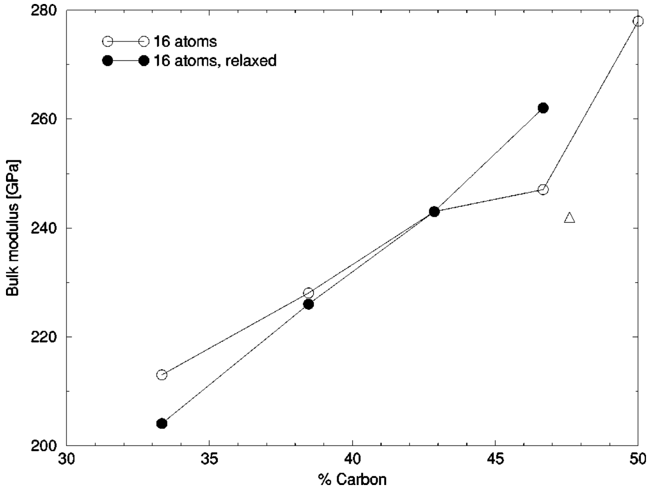

FIG. 10. The bulk moduli for the stoichiometries studied as a function of carbon content. The experimental value is indicated by a triangle.

(i) The total picture obtained from the different geometries used, clearly shows the importance of the choice for the vacancy positions in the substoichiometric structures with a large variation in both energy of formation and equilibrium volume being found for different choices. The choices that generally have lower energy are found to be those that minimize the number of titanium atoms having more than the average number of vacancies as nearest neighbors, i.e., it is more favorable to have two titanium atoms with two nearest-neighbor vacancies than one with one and the other with three.

(ii) The effect of local relaxations of the titanium atoms around one vacancy is seen to be an outward relaxation, in agreement with experiment and previous studies, and the magnitude of the relaxation is dependent on the number of vacancy neighbors. This outward relaxation can be understood as a result of the highly directional *p-d* bonds in this compound and results in an increase of the lattice parameter. If a larger supercell is used the next-nearest-neighbor carbon atoms are found to relax towards the vacancy by 0.026 Å and the outward relaxation of the titanium atoms increases from 0.049 Å to 0.069 Å.

(iii) In this study a very small decrease of the lattice parameter over a large range of stoichiometry, TiC - Ti_2C, of the order of 1% is found. This is in accordance with experiment where the lattice parameter also changes with 1% over this range. Previous theoretical studies have found a small increase or decrease, depending on vacancy positions, of the lattice parameter at small concentrations of vacancies. Though the inclusion of local relaxations around the vacancies results in an increase of the theoretical lattice parameters, the theoretical lattice parameters found in this study do not indicate that the lattice parameter of any of the substoichiometric phases is larger than that of stoichiometric TiC. In order to achieve an overall increase of the lattice parameter when introducing vacancies in the carbon sublattice the outward relaxation of the Ti atoms must be larger than that found in our study. Whether this is a shortcoming of our present method, perhaps due to supercell size, or representing the correct physical situation is not clear.

(iv) The effects of local relaxations around the vacancies are found to be instrumental in explaining the phase stabilities of the substoichiometric titanium carbides, where only the fully relaxed energy curves show the correct energy of formation minimum at off-stoichiometric TiC_{1-x}, with $0.94<x<1.00$.

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