

# VACANCY ORDERING AND NON-STOICHIOMETRY IN $\text{TiC}_{1-x}\square_x$ and $\text{TiN}_{1-x}\square_x$

Gus L. W. Hart,<sup>1</sup> Barry M. Klein,<sup>2</sup> and Shanadeen Begay<sup>3</sup>

## 1. INTRODUCTION

Nearly two centuries ago, Dalton discovered that most compound materials occur in precise integer stoichiometry.[1] As pointed out by Lewis,[2] the existence of this integer ratio of the constituent atoms in a compound (or even in elemental solids) results from the fact that atoms bonded in a solid tend to donate, accept, or share an integer number of electrons with their neighbors. Although deviations from precise stoichiometry (due to intrinsic vacancies or interstitials) are known to exist, such deviations are small and are *entropically* stabilized and thus will disappear as  $T \rightarrow 0$ . However, there exist several classes of binary compounds for which the existence of vacancies actually *reduces* the free energy, even at low temperatures, and for which the deviations can be astonishingly large, 50% or more. Categorizing these materials by their properties and behavior, vacancy ordering and complexes, homogeneity range etc., one can mention three classes of these “intrinsically” non-stoichiometric materials: (i) transition metal oxides (such as VO or TiO), (ii) transition metal nitrides and carbides (such as HfC, NbN, etc.), and (iii) early transition metal chalcogenides[3] (such as ScS or ZrSe). All three groups have been studied extensively but the first two groups have garnered more interest because of the broad range of their technological applications.[4]

In this paper we focus on two materials in the second group, namely TiC and TiN. Both of these materials, along with the others in their class, have been studied extensively (see, e.g., Refs. [4–8] and references therein); they are of particular interest for their industrial applications as well as for their basic science appeal owing to their unusual properties (e.g., hardness and high melting temperatures). The materials in this class are characterized by strong mechanical properties and high melting temperatures. Titanium carbide, for exam-

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<sup>1</sup>Gus Hart, Department of Physics and Astronomy, Northern Arizona University, Flagstaff AZ 86011-6010, gus.hart@nau.edu

<sup>2</sup>Barry M. Klein, Department of Physics, University of California, Davis CA 95616, bmklein@ucdavis.edu

<sup>3</sup>Shanadeen Begay, Northern Arizona University, Flagstaff AZ 86011-6010, scb8@dana.ucc.nau.edu

ple, is a major component in cemented carbides and is widely used for surface coatings.

We have studied how the electronic structure of the TiC and TiN systems stabilizes such a large range of non-stoichiometry ( $0 \leq x \lesssim 50\%$ ), leading to the predicted low temperature, vacancy-ordered structures. Although the low temperature structures are not likely to be realized experimentally due to the sluggish diffusion, understanding the ordering tendencies gives insight into the chemical mechanisms responsible for the non-stoichiometry and how the mechanical properties are affected by the existence of vacancies.

Since the vacancy configuration, that is the crystal structures, for these materials are not known experimentally and the vacancy concentration-dependent behavior is difficult to guess based on past experience, we cannot resort to the prevalent but unreliable approach of assuming a limited set of “intuitive” trial structures and then performing first-principles calculations to determine the lowest energy structure in the trial set. The limitation of this approach is particularly acute in vacancy-ordering compounds where the ground state structures tend to have relatively large unit cells and low crystallographic symmetry. Many times in the literature, conclusions have been drawn from first-principles calculations of high-symmetry, small-unit-cell structures. Though convenient from the point of view of computational cost, these structures often turn out to have energies that are far above that of the true ground states and thus do not represent the true “chemistry” responsible for the formation and ordering of vacancies in the compound. This approach of selective sampling is driven by the high computational cost of these calculations and the prohibitive cost of exploring the all possible configurations.

Performing calculations for a material when the thermodynamic states are actually not known and for which large-unit-cell structures are common presents a formidable problem for the conventional first-principles approach. The difficulty arises both from the size of unit cells that must be treated and the literally more-than-astronomical number of configurations that must be considered. For this reason, we have used a cluster expansion (CE) method[9–14] in which first principles, total-energy calculations for a relatively small database of ordered superstructures is mapped onto a 3D Ising model. Once this CE Hamiltonian has been successfully constructed, efficient and accurate ground state search techniques (simulated annealing, direct enumeration, genetic algorithms, parallel tempering) can be applied, without guessing, to identify the minimum-energy configurations and Monte Carlo simulations can be used to study finite-temperature effects. Once the low energy structures are determined, we analyze their electronic structure using the LDA/GGA pseudopotential approach. Thus we have a significant advantage over the conventional approach of rounding up a few suspect structures because we analyze those structures that are actually energetically stable, without limiting ourselves to small unit cells or artificially high symmetry structures.

## 2. THE CLUSTER EXPANSION

### 2.1. General Formalism

The cluster expansion (CE) expresses the excess energy of any lattice configuration  $\sigma$  (a particular occupation of the  $N$  lattice sites by A or B atoms) as

$$\Delta H_{\text{CE}}(\sigma) = J_0 + \sum_f^{N_f} D_f \bar{\Pi}_f(\sigma) J_f \quad (1)$$

where  $J_f$  is the effective atom-atom interaction for cluster type  $f$  (pair, triangle, tetrahedron, etc.),  $N_f$  is the number of clusters of type  $f$  in configuration  $\sigma$ ,  $D_f$  is the number of

clusters of type  $f$  per lattice site, and  $\bar{\Pi}_f$  are the averaged spin products[15] for configuration  $\sigma$ . In the case of  $\text{TiC/N}_{1-x}\square_x$ , the up and down “spins” represent the carbon/nitrogen atom and its vacancy. Because it is present on every anion site and does not constitute a configurational degree of freedom, the titanium atom is not explicitly included in the expansion (but it is included, of course, in the LDA calculations of the total energy.)

Sanchez, Ducastelle, and Gratias showed[9] that a single set of interactions can exactly reproduce the directly calculated total energies of all possible configurations  $\sigma$ . Of course, this is only true for the untruncated expansion ( $N_f = 2N$ ) so the validity of the truncated expansion naturally depends on the vanishing nature of higher order terms. The  $J$ 's are determined by fitting the expansion  $\Delta H_{\text{CE}}(\sigma)$  to the excess total energies  $\Delta H_{\text{LDA}}(\sigma)$  of a set of  $N_\sigma$  “input structures” calculated by first-principles methods. We use the pseudopotential planewave method,[16] as implemented in the VASP[17, 18] code. In each case, we relax both cell-external and cell-internal degrees of freedom to obtain  $\Delta H_{\text{LDA}}(\sigma)$ . The interactions were chosen by first eliminating from the fit several of the input structures and choosing the interactions that result in an accurate fit to the structures retained as well as accurate predictions for the eliminated structures. The process is repeated using different sets of eliminated structures to ensure a set of interactions that work well *generally*.<sup>4</sup> The process of determining a good fit is discussed in detail in Ref. [13].

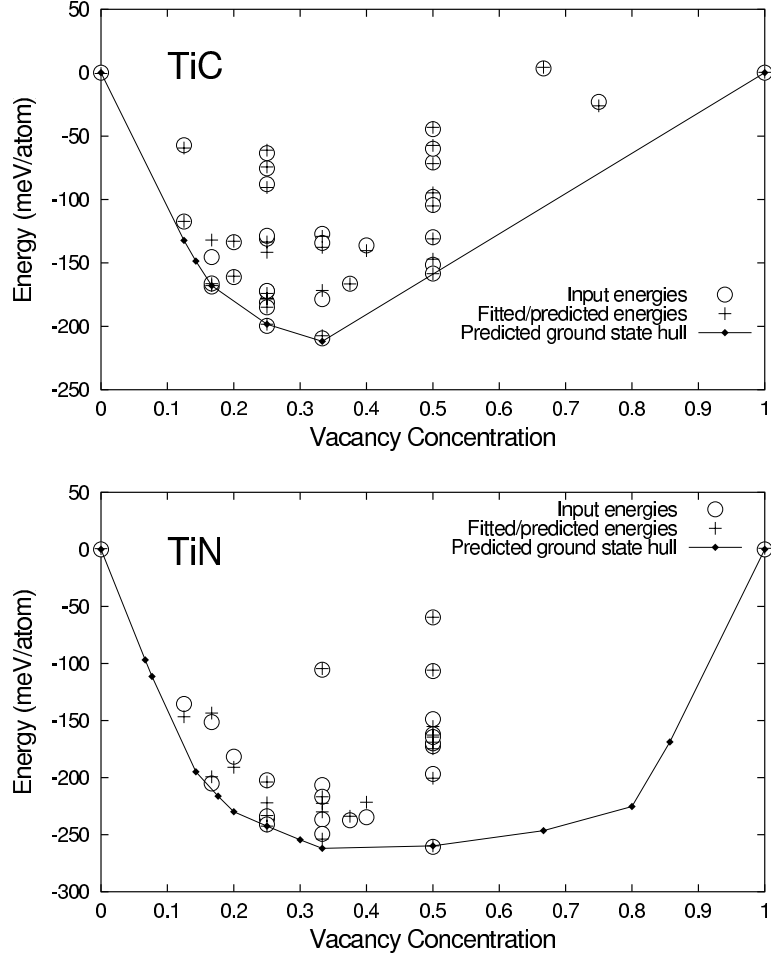
## 2.2. Ground State Searches

The most common way to find the thermodynamically stable ground states of alloy systems modeled via cluster expansion approaches is Monte Carlo-based searches (i.e., simulated annealing).[20, 21] Although simulated annealing has been quite successful for simple intermetallic and semiconductor alloys,[22–26] such an approach does not guarantee that the states found are *global* minima of the energy functional (they may not be true ground states).

In our studies, we have found that, although the simulated annealing (SA) approach to ground state searches is useful in many cases, there are cases (non-stoichiometric systems in particular) where a complementary search technique is helpful, or in some cases, essential. The SA approach suffers from three problems. (1) Critical slowing down: When the simulation suffers from this problem, the necessary computer time to reach an answer becomes prohibitive. This problem seems to be particularly acute for the cases (such as the refractory carbide and nitride compounds) where the ordered states have relatively large unit cells. (2) Failure to converge: In some cases, the low energy states at a given concentration (including the ground state) are so closely spaced (in energy) that the SA approach fails to converge. (3) False ground states: Occasionally we have found ground states with SA that appear to be robust, when in fact, a direct enumeration of ground states (restricted to a limited cell size, of course) will turn up a ground state *lower* in energy than that found by the SA approach.

The most robust solution to these obstacles is to perform the ground state searches by direct, exhaustive enumeration, that is, a direct brute-force determination of all possible configurations. Formally, however, such an approach is impossible (for very large unit cells) because there are a prohibitive number of states to enumerate. Direct enumeration is, however, very useful when applied to relative small unit cell sizes (about 16 to 20 atoms)

<sup>4</sup>The fit is optimized by requiring the “maximum smoothness criteria (Eqs. 24–26 of Ref. [19]). The parameters  $t$  and  $\lambda$  are simultaneously optimized to yield both a good fit for fitted structures and accurate predictions for “eliminated” structures.

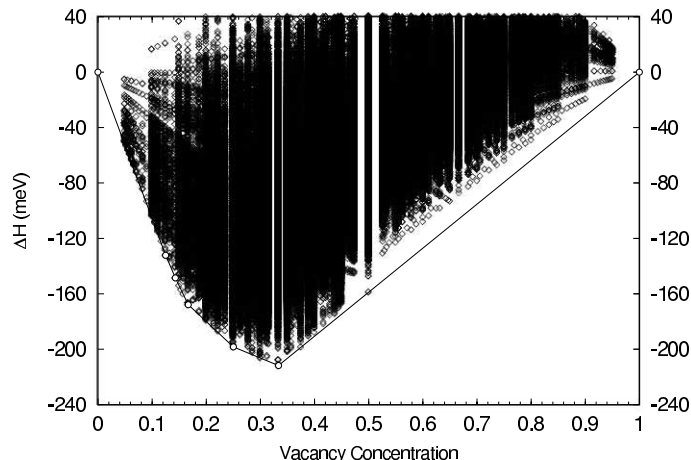


**Figure 1:** Cluster expansion fits for TiC (top) and TiN (bottom). CE-predicted values are very close to the LDA values, indicating an accurate fit. The solid lines show the ground state hull and the solid points show the ground states. The ground states are discussed in Sec. 3.

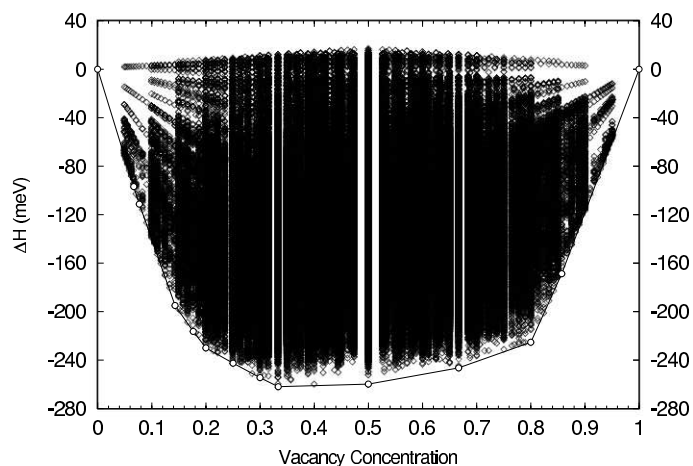
and we have applied this method in this work. We have enumerated all possible configurations for unit cell sizes  $\leq 20$  atoms/cell using the method of Ferreira et al.[27] There are more than 3 million unique configurations for the fcc lattice in this size range. Results of ground state searches using this direct enumeration method are shown in the following section.

### 2.3. Cluster Expansion Fits for $\text{TiC}_{1-x}\square_x$ and $\text{TiN}_{1-x}\square_x$

Figure 1 demonstrates the accuracy of the fits we developed for the case of  $\text{TiC}_{1-x}\square_x$  and  $\text{TiN}_{1-x}\square_x$  using the procedure discussed in Sec. 2.1. Ultimately, we included about 30 first-principles energies in the fitting. The CE fitting parameters were checked not only for *fitting* accuracy (how well the energies of the input structures are reproduced) but also for their accuracy in *prediction* (how accurately the energies of structures *not* included in the



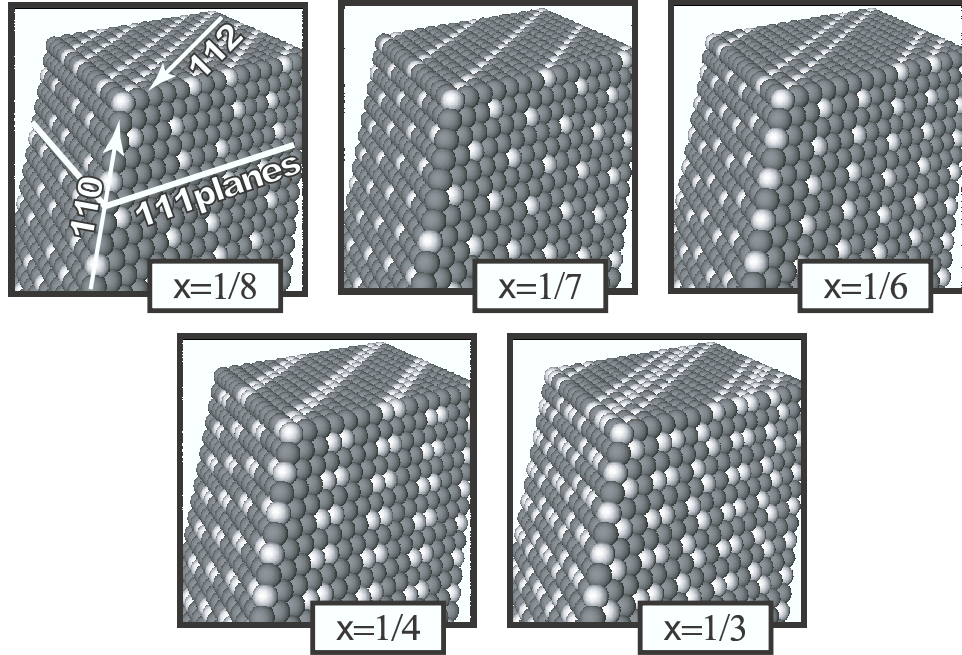
**Figure 2:** Ground state search results (via direct enumeration) for TiC. The five stable configurations occur at concentrations  $x \leq 1/3$ . However, the lowest configuration at  $x = 1/2$  is very close to the ground state hull and may actually be stabilized by effects not considered in the model (such as vibrational entropy).



**Figure 3:** Ground state search results (via direct enumeration) for TiN. In this case the ground states cover a broader vacancy concentration range than for TiC. Also, the formation enthalpies are about 25% lower than for the case of TiC.

fit are predicted by the CE). When a fit is accurate both for fitting and for predictions, we refer to that fit as *robust*. As mentioned above, an in-depth discussion of how to determine the optimum interaction energies (i.e., the fitting parameters) is given in Ref. [13].

The results displayed in Fig. 2 show that the input energies (calculated via first principles) are reproduced very accurately by the CE; in most cases, the error is only a few percent. These robust fits were obtained with  $\sim 17$  pair and 7 three-body and four-body



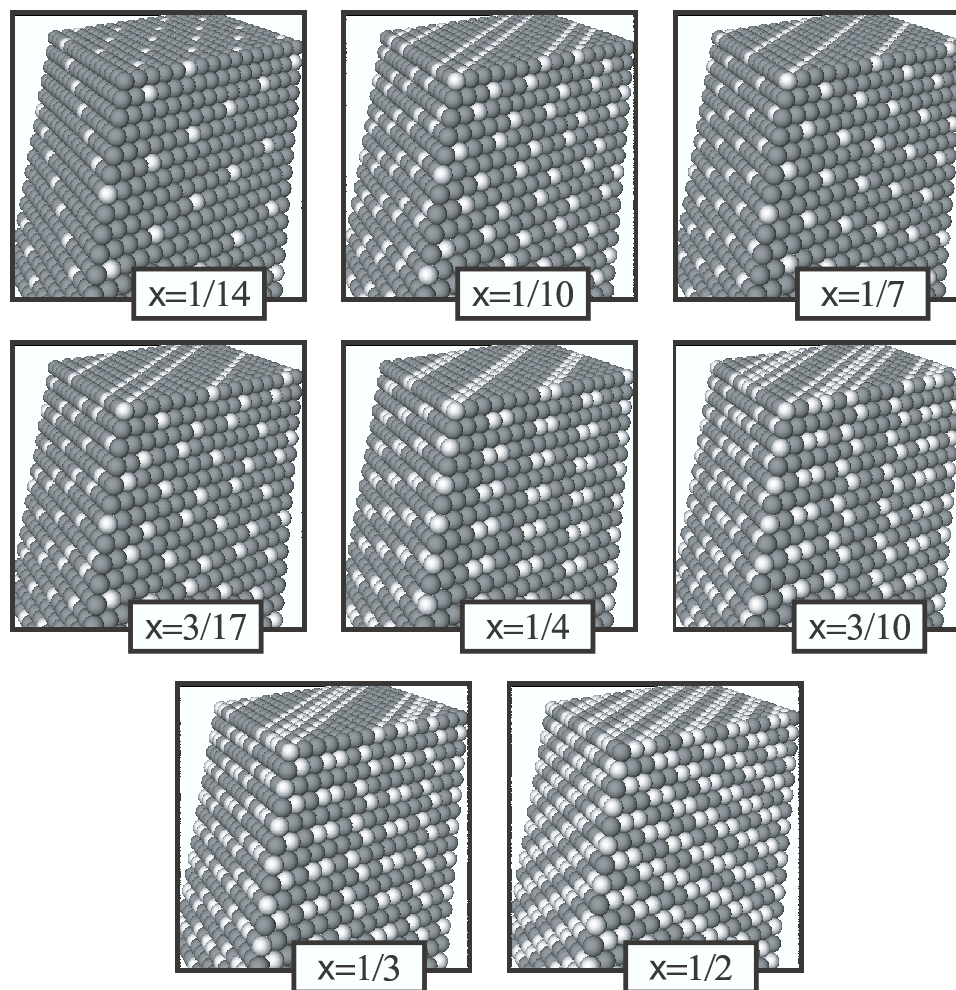
**Figure 4:** Ground state structures for TiC. Only the occupation of the carbon sites is shown (black occupied, white unoccupied); the titanium atoms are not shown. Note that the pictures are not visualizations of a cubic supercell but rather stacked (111) planes of the FCC lattice. Note the common motif of (112) rows of vacancies in each (111) plane and that planes are generally stacked so that rows of alternating vacancies are formed in the (110) direction.

interactions. Typical fitting and prediction errors (rms) for TiC and TiN are  $\sim 4$  meV/atom, whereas the average  $\Delta H$  is approximately  $-150$  and  $-200$  meV/atom for TiC and TiN, respectively. In the simulations discussed below, we used a final fit that included *all* of the input structures.

### 3. RESULTS AND DISCUSSION

Figure 2 shows a ground state search (via direct enumeration) of the ordered vacancy states for the case of TiC. Our search finds five ground states (stable vacancy-ordered configurations). The most stable structure occurs at  $x = 1/3$ . However, the lowest energy configuration at  $x = 1/2$  is so near the ground state hull that it may actually be realized if effects not included in our model (such as vibrational entropy) are properly taken into account. Consequently, the homogeneity range for  $\text{TiC}_{1-x}\square_x$  may actually be 0–50% rather than 0–33%.

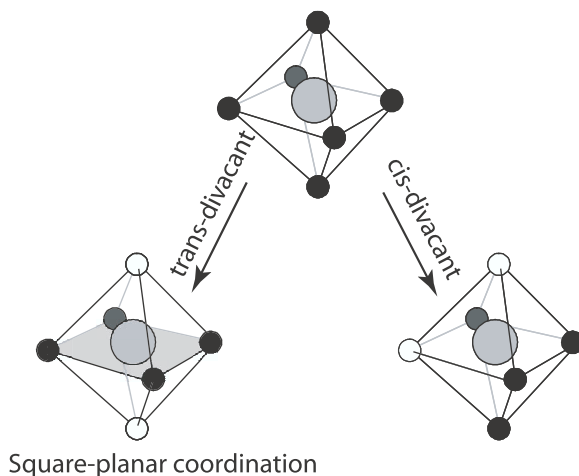
Figure 3 shows the same information as Fig. 2 except for TiN. The most stable structure again occurs at a vacancy concentration of  $x = 1/3$  but the ground state at  $x = 1/2$  is almost as low in energy. In all, twelve ground states are predicted by the CE. The predicted homogeneity range of  $\text{TiN}_{1-x}\square_x$  is much larger in this case. This is in qualitative agreement with experimental observations which show a homogeneity range of  $0 \leq x \lesssim 52\%$  for TiC and  $0 \leq x \lesssim 62\%$  for TiN.[3] In fact, for the class of transition-metal carbide



**Figure 5:** Ground state structures for TiN. See the caption for Fig. 4 for labeling of states and a description of the common motifs observed. TiN yields more ground state structures than TiC, due in part to the larger homogeneity range.

and nitride binary compounds that exhibit intrinsic non-stoichiometry, it is always the case that the nitride has a larger homogeneity range than the corresponding carbide.

The most striking result of the ground state searches is the common motifs that are observed. The motifs are the same for both TiC and TiN and exist across a large concentration range in each system. In Figures 4 and 5, the ground states are visualized as a stacking of (111) planes of the FCC lattice. Within the (111) planes, vacancies are arranged in (112) rows (i.e., adjacent vacancies are on third nearest neighbor sites). Also, the rows are often stacked so that, in the (110) direction, vacancies occur on every other site (fourth nearest neighbor distance). The motif of (112) vacancy rows persists even for low vacancy concentrations, i.e., configurations which do not maximize the inter-vacancy distance are the rule. This implies that vacancy-vacancy interactions at some distance beyond first nearest neighbors become attractive.



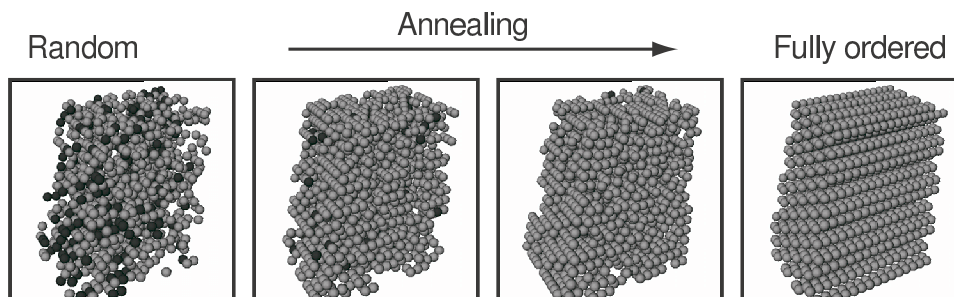
**Figure 6:** Titanium octahedra in TiC and TiN. In the NaCl structure, titanium atoms (large gray spheres) are surrounded by six carbon (or nitrogen) atoms (black spheres). If two vacancies (white spheres) are present, only two arrangements are possible: vacancies on opposite corners (trans-divacant) or vacancies as nearest neighbors (cis-divacant). If the octahedron is trans-divacant, then the titanium atom in the center will be square-planar coordinated by the remaining non-metal atoms.

The structure at  $x = 1/3$  is identical for both TiC and TiN. This structure is known as “Sc<sub>2</sub>S<sub>3</sub>.”[28] (ScS is also a non-stoichiometric binary system, albeit with vacancies on the metal, rather than non-metal, site.) The Sc<sub>2</sub>S<sub>3</sub> structure has a large unit cell (12 Sc sites and 12 S/□ sites) and occurs very commonly in the early transition-metal chalcogenide binary compounds (which are also intrinsically non-stoichiometric).[3] This is intriguing: despite the chemical differences between ScS and TiC/N and the fact that vacancies occur on the opposite sublattice (metal vs. non-metal), TiC and TiN display a set of vacancy-ordered configurations very similar to ScS and other transition-metal chalcogenide binary compounds. Indeed, at several concentrations, the configurations are identical.

We also note that in most cases, the size of the unit cells of the ground states are relatively large (12–16 C/N sites/cell); larger than the unit cells of intermetallic compounds (typically 4–8 sites/cell). And the unit cells have relatively low symmetry.

Owing to the NaCl structure, each atom in these binary compounds is six-fold coordinated with its nearest neighbors (which are of the opposite atomic type). One can imagine a octahedron around the titanium atoms where carbon (or nitrogen) atoms sit on the six corners of the octahedron, as shown in the top of Fig. 6. If the vacancy concentration is  $x \leq 1/3$  then the average number of vacancies per octahedron will be  $\leq 2$ . Similarly, for  $x \leq 1/6$  the number of vacancies per octahedra will be  $\leq 1$ . If we examine the predicted ground state structures from the point of view of this picture of the octahedra around the metal atoms, we uncover two noteworthy facts: (i) generally, these structures minimize the number of vacancies per octahedra for a given concentration, e.g., at  $x = 1/3$  each and every octahedron has exactly two vacancies, and (ii) when an octahedron has two vacancies present, the vacancies are *never* present on opposite corners of the octahedra, rather the two vacancies are always nearest neighbors.





**Figure 7:** Simulated annealing simulation of TiC at  $x = 1/4$ . Only the titanium atoms in *divacant* octahedra are shown; carbon atoms and other titanium atoms are not shown. Titanium atoms in “cis-divacant” octahedra are shown in gray and those in “trans-divacant” octahedra are shown in black. Note that *trans*-divacant Ti octahedra disappear well before significant long-range order is observed.

The first observation implies that vacancies are repulsive for first and second nearest neighbor distances but the second observation shows that a *first*-nearest-neighbor coordination of the vacancies is far more energetically favorable than a *second*-nearest-neighbor coordination. For the case of ScS, Burdett pointed out[29] that when scandium vacancies are on opposite corners of the octahedron (“trans-divacant” arrangement) the sulfur atom becomes square-planar coordinated (see Fig. 6), a situation never observed in solid state chemistry. Without a single exception, all of the vacancy-ordered structures presented here (as well as those of ScS in Ref. [30]) have this so-called “cis-divacant” arrangement for all double vacancy octahedra.

Using the CE Hamiltonian in Monte Carlo simulations, we found that the trans-divacant octahedra naturally occurring in a random arrangement of vacancies are quickly replaced by cis-divacant octahedra. In fact, most of the trans-divacant octahedra are eliminated well before the structure acquires significant long range order, as shown in Fig. 7.

In a previous study of non-stoichiometry in ScS, [30] an analysis of the charge densities and partial densities of states for a series of low-energy structures with increasing vacancy concentration revealed very clearly the mechanism of intrinsic non-stoichiometry in that system. Despite the very obvious similarities of the ground states in these two systems compared to those of ScS, the details of the mechanism for non-stoichiometry appears to be different. An analysis of the partial densities of states(not shown here) for non-stoichiometric TiC and TiN did not reveal a mechanism for vacancy formation similar to that found for ScS—a somewhat puzzling result given the fact that the ground states in ScS are so closely related to those in TiC/N. At this point, we have not been able to determine the electronic mechanism that drives the formation of vacancies in TiC and TiN. This topic is a focus of our current research and will be discussed in a future publication.

#### 4. SUMMARY

Using a database of first-principles calculated formation enthalpies, we constructed cluster expansions[9–14] for the vacancy systems TiC and TiN. The ground state hulls predicted by the cluster expansion are consistent with the experimentally known homogeneity ranges[3] for these two compounds. Using a direct enumeration method,[27] we determined the ( $T = 0$ ) ground state structures and found that they are very similar in these two systems. A common feature of the ground states is that vacancies prefer to arrange themselves in

(112) rows, almost independent of the vacancy concentration. In all of the ground states, vacancies completely avoid any arrangement that would lead to square planar coordination of the titanium atoms, even if this results in nearest-neighbor vacancies. Surprisingly, the ground states we discovered and their common structural motifs are very similar (often identical) to those discovered in the ScS system.[30] However, an analysis of the charge density and densities-of-states for TiC and TiN did not indicate a mechanism for vacancy formation similar to that found for ScS despite the very obvious structural similarities of the stable configurations in all three systems. The precise electronic mechanism driving the formation of vacancies is still unclear and is the subject of ongoing research.

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