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First-principles study of effective cluster interactions and enthalpies of formation of substoichiometric VC_{1-x}

V. Ozoliņš and J. Häglund
Department of Theoretical Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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We have performed extensive first-principles electronic structure calculations on a series of ordered VC_{1-x} compounds using the full-potential linear-muffin-tin-orbitals method. The results are fitted to equations of state and volume-dependent effective cluster interactions (ECI's) are determined. A set of eight composition-independent ECI's including pair interactions up to the third-nearest neighbors as well as some multiplet clusters are found to reproduce the total electronic energies of all ordered VC_{1-x} compounds within 1 mRy/atom. These ECI's are used to derive the enthalpy of formation at 0 K, $\Delta^0 H^{\text{dis}}(x)$, for VC_{1-x} with a completely disordered vacancy configuration. $\Delta^0 H^{\text{dis}}(x)$ is higher than $\Delta^0 H[\text{VC}]$ for all vacancy concentrations $x \neq 0$. The energy gain due to ordering is approximately 10 mRy/V atom. This energy is enough to yield enthalpies of formation of some ordered structures (e.g., V_8C_7 and V_6C_5) that are below the enthalpy of formation for VC. We conclude that the ground state of VC_{1-x} at zero temperature occurs for $x \neq 0$. Lattice relaxations around vacant sites are not accounted for by our ECI's. These will further decrease the total energy of VC_{1-x} and thus stabilize the vacancies. We present a simple band-filling model which qualitatively explains the limited stability range of vacancy formation.

I. INTRODUCTION

There has been a considerable effort to understand the exceptional physical properties of transition-metal (TM) carbides in the NaCl structure. Numerous calculations of electronic band structures[1–10] for both stoichiometric and substoichiometric compounds have been carried out. It is well established[10–14] that the large cohesive energy of the carbides in the first part of the transition-metal series is due to strong covalent metal-nonmetal bonds formed by overlapping metal *d* and carbon *p* orbitals. Most of these carbides contain a considerable amount of vacancies in the carbon sublattice,[15] and some of them (e.g., VC) have never been synthesized in a stoichiometric form. Several authors have discussed these effects. Zhukov*et al.*[13] argue that TM carbides contain vacancies because they are prepared at high temperatures where vacancy formation is favored by an increased configurational entropy. They further suggest that high energy barriers for vacancy migration prevent the system from reaching stoichiometry at low temperatures. A different explanation has been given by Klein, Papaconstantopoulos, and Boyer.[5] These authors argue that slow diffusion rates at the formation temperatures of TM carbides inhibit penetration of carbon atoms into the metal lattice. Huisman, Carlsson, and Gelatt[16] have proposed a simple model, suggesting that vacancy formation in some systems may be energetically favored by electronic states induced below the Fermi level. Particularly, they show that the energy of vacancy formation is negative in TiO and positive in TiC which agrees well with experimental observations. In conclusion, there seems to be no general agreement on the reasons why it is so difficult (if at all possible) to prepare certain TM carbides in a stoichiometric phase.

A common feature of the stoichiometric TM carbides in the NaCl structure is a pronounced minimum in the electronic density of states (DOS) separating bonding and antibonding states.[3,10,11,14] Vacancies in the carbon sublattice cause the appearance of so-called vacancy peaks in the region of minimum DOS.[3,4,7,10] These peaks correspond to states of *s*- and *p*-like symmetry on the vacant site formed by overlapping *d* orbitals from the surrounding octahedron of TM atoms. These states and vacancy-induced charge redistributions have been studied in detail by Redinger *et al.*[10] for a hypothetic $Ti_4C_3\Box$ ($\Box$ = vacant site) compound using a conventional band-structure technique. These authors argue that new metal *d*-*d* bonds are formed and that the existing *p*-*d* bonds are strengthened by additional charge transfer from transition metal to carbon atoms. Marksteiner *et al.*[7] performed calculations on disordered substoichiometric titanium and vanadium carbides and nitrides using the Korringa-Kohn-Rostoker–coherent-potential-approximation (KKR-CPA) and the Korringa-Kohn-Rostoker–Green's-function (KKR-GF) methods. They conclude that the vacancy peaks are shifted upwards and that the Fermi energy is lowered by an increased vacancy concentration. Cluster calculations,[9] performed for 27 and 53 atom clusters of NbC revealed the appearance of additional peaks in the electronic DOS between bonding and antibonding states. However, Pickett, Klein, and Zeller[8] argue that the energies of these peaks are substantially affected by the size of the chosen cluster, and for small clusters surface effects may have considerable influence. This indicates that vacancies introduce spatially extended electronic states. Pickett, Klein, and Zeller[8] further suggest that the interaction and ordering of va-

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cancies may be important for understanding the substoichiometry of TM carbides.

Several authors[17–20] have noted that the carbon-vacancy sublattice in a NaCl-structure compound $\mathrm{MC}_{1-x}\Box_x$ is formally analogous to a fcc binary alloy $A_{1-x}B_x$ suggesting that its statistical properties can be described by a generalized Ising spin model. To our knowledge, only carbon-vacancy pair interactions have been calculated, either by fitting to experimental data[17] or by using the generalized perturbation method (GPM).[18–21] These studies have successfully described and classified the structural stabilities of TM carbides and nitrides, but they have not provided explanations for the almost universal nonstoichiometry of these compounds.

In this paper we study the enthalpies of formation of substoichiometric VC_{1-x} using recent developments in cluster expansion (CE) methods[22–29] for configuration-dependent properties of substitutional alloys. The energetics of substitutional alloys in the CE approach are described by a generalized Ising Hamiltonian with coupling constants derived from total-energy calculations on a set of periodic structures.[24] We use the full-potential linear-muffin-tin-orbitals[30] (FP-LMTO) method to determine total electronic energies of ten VC_{1-x} compounds with ordered vacancy configurations. From the calculated total energies, we obtain the coupling constants for a generalized Ising Hamiltonian (effective cluster interactions or ECI's) and we predict the formation enthalpies of other ordered phases and of disordered VC_{1-x} with a completely random distribution of vacancies. We compare our results with estimates[31,32] obtained using the empirical two-sublattice model for substitutional solutions.[33] Finally, we qualitatively explain the variation in the enthalpy of formation, using a simple band-filling model.

The paper is organized as follows. The cluster expansion of the total energy is reviewed in Sec. II. In Sec. III we comment on the details of our *ab initio* electronic band-structure calculations. Section IV presents results from our electronic structure calculations, as well as calculated ECI's and enthalpies of formation. Our results are discussed in Sec. V and the paper ends with a summary in Sec. VI.

II. ECI EXPANSION OF THE TOTAL ENERGY

Consider a binary alloy A_xB_{1-x} where atoms A and B reside on a fixed lattice with N sites. Spinlike variables σ_i are assigned to each site i. σ_i takes the values $+1$ or -1, depending on whether the site i is occupied by an atom A or B. Thus, any configuration of the lattice may be characterized by a vector in N-dimensional space of discrete spin variables $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \ldots, \sigma_N)$. We now define clusters α, containing n lattice sites. Cluster functions Φ_α are written as products of spin variables,

$$\Phi_\alpha(\sigma_{p_1}, \sigma_{p_2}, \ldots, \sigma_{p_n}) = \sigma_{p_1}\sigma_{p_2}\ldots\sigma_{p_n}, \qquad (1)$$
$$\alpha \equiv (p_1, p_2, \ldots, p_n).$$

For the more general case of an M-component system, Sanchez, Ducastelle, and Gratias[23] have shown that the functions Φ_α form an orthogonal and complete basis set in the configuration space of the lattice with respect to a scalar product defined as the trace over all possible configurations $\boldsymbol{\sigma}$.

Any configuration-dependent property of the system may be expressed as a cluster expansion.[23] For instance, the total energy can be written

$$E(\boldsymbol{\sigma}) = E_0 + \sum_\alpha E_\alpha \Phi_\alpha(\boldsymbol{\sigma}), \qquad (2)$$

where α runs over all nonempty clusters. The coefficients E_α are referred to as *effective cluster interactions* (ECI's). Among the 2^N coefficients E_α, those of clusters equivalent by the symmetry of the disordered lattice are equal.[23] This allows us to rewrite Eq. (2) as

$$\varepsilon(\boldsymbol{\sigma}) \equiv \frac{1}{N}E(\sigma) = \varepsilon_0 + \sum_\alpha E_\alpha m_\alpha \overline{\Phi}_\alpha(\boldsymbol{\sigma}), \qquad (3)$$

where the sum is taken only over symmetry-distinct clusters. m_α is the number of symmetry-related clusters per lattice site and the bar over the cluster functions denotes an average over all clusters of type α.

The cluster expansion in Eq. (3) can be used to predict the total energy of any structure using only a small number ($\approx$ 10) of concentration-independent ECI's. Connolly and Williams[24] noted that E_α may be obtained from total-energy calculations on a set of periodic structures $\{\phi\}$. The averaged cluster functions $\overline{\Phi}_\alpha$ in Eq. (3) can be readily calculated for periodic configurations and the ECI's are found by inverting Eq. (3). Since the total energies are obtained as functions of volume, the cluster energies $E_\alpha(V)$ also become volume dependent. If the number of periodic structures is larger than the number of ECI's, a least-squares fit to the calculated set of energies must be performed. Let Z be the number of periodic structures and L the number of ECI's. As pointed out by several authors,[25,27,28] a proper weighting and choice of ECI's is necessary to avoid sensitivity to the errors in calculated total energies. Lu *et al.*[27] proposed the following form for the weighted variance:

$$w = \sum_{\{\phi\}}^{Z} \omega_\phi \left[\varepsilon(\phi, V) - \sum_\alpha^{L} m_\alpha E_\alpha(V)\overline{\Phi}_\alpha(\phi)\right]^2, \qquad (4)$$

which has to be minimized with respect to the ECI's $E_\alpha(V)$. The weights ω_ϕ for a fcc lattice are given by[27]

$$\omega_\phi = 48\frac{N_C(\phi)}{N_G(\phi)}, \qquad (5)$$

where $N_C(\phi)$ is the number of atoms per unit cell and $N_G(\phi)$ is the number of point-group operations of the structure ϕ.

Ideally, one should try several sets of cluster interactions and choose the one that minimizes the weighted variance in Eq. (4). If several sets of ECI's give an equally good fit to calculated $E_\alpha(V)$, the one with the highest degree of orthogonality should be preferred.[28] Asta *et al.*

have suggested the following orthogonality criterion:[28]

$$\mathcal{O} = \frac{1}{2Z(Z-1)} \sum_{\{\phi\}}^{Z} \sum_{\{\phi' \neq \phi\}}^{Z} \sum_{\alpha}^{L} \hat{\overline{\Phi}}_\alpha(\phi)\hat{\overline{\Phi}}_\alpha(\phi'), \tag{6}$$

$$\hat{\overline{\Phi}}_\alpha(\phi) = \frac{\overline{\Phi}_\alpha(\phi)}{\sqrt{\sum_\alpha^L \left[\overline{\Phi}_\alpha(\phi)\right]^2}}. \tag{7}$$

$\mathcal{O}$ is zero for an orthogonal set of cluster functions $\overline{\Phi}_\alpha(\phi)$ and its maximum value is 1.

III. ELECTRONIC STRUCTURE CALCULATIONS

We have used a full-potential version of the linear-muffin-tin-orbitals (LMTO) method.[30] In our calculations, the muffin-tin spheres are nonoverlapping and the contributions from the interstitial region are accounted for by expanding the products of Hankel functions in a series of atom-centered Hankels of different kinetic energies. The coefficients of this expansion are chosen so as to match the values and slopes of the products on the surface of all muffin-tin spheres. This approach requires a good sphere packing for the expansion of interstitial functions and in open structures one has to introduce additional empty spheres. Electronic exchange and correlation contributions to the total energy were obtained from the local-density functional,[34] calculated by Ceperley and Alder[35] and parametrized by Vosko, Wilk, and Nusair.[36]

Muffin-tin radii around vanadium and carbon sites were set to be equal and slightly smaller than the half distance between V and C. Two LMTO envelopes with tail energies -0.001 Ry and -1.0 Ry were used as a basis set for the valence panel. We included *s,p,d* orbitals in both envelopes for all sites. The addition of *f* orbitals to the first envelope of V lowered the total energy by 3 mRy per V atom. A further increase of the basis set did not change the total energy appreciably. Two Hankel functions of kinetic energies -1.0 Ry and -3.0 Ry were used for the interstitial fit. The effect on the total energy from a 25% change in the energies of the fit functions amounted to less than 1 mRy. The free-core approach was adopted, revealing the need to treat vanadium 3*s* and 3*p* orbitals as semicore states forming narrow bands well below the energy window of the valence panel. Separate matrix diagonalizations for each panel were performed at each iteration. Whenever possible, we used the same unit cell and **k**-point mesh for all compositions in order to ensure maximum cancellation of numerical errors and to obtain accurate energy differences. Murnaghan's equation of state was used to interpolate the volume dependence of the total energy and to determine bulk moduli and equilibrium lattice constants.

Calculations for graphite were performed with additional empty spheres introduced into the centers of honeycomb cells on the lattice planes perpendicular to the *c* axis and halfway between these planes. Two envelopes with *s*, *p*, and *d* orbitals on each site yielded convergence to within 1 mRy with respect to the basis set. The c/a ratio was taken at the experimental value of 2.4.

IV. RESULTS

We have performed electronic structure and total-energy calculations for 10 ordered VC_{1-x} compounds. The crystal structures of these compounds were obtained by decorating the vertices of a stoichiometric VC conventional cell and a double-tetrahedron–octahedron cluster (see Fig. 1) with vacant sites. In Table I we list our calculated equilibrium lattice constants and bulk moduli. Furthermore, we give the enthalpies of formation, $\Delta^0 H$, with respect to fcc V and graphite, defined through

$$\Delta^0 H[VC_{1-x}] = E^{\rm tot}[VC_{1-x}] - E^{\rm tot}[V_{\rm fcc}] - (1-x)E^{\rm tot}[\text{graphite}]. \tag{8}$$

The lattice parameters given in Table I are approximately 5% below experimental values.[37] This error can be attributed to the local-density approximation (LDA). Figure 2 shows DOS curves for stoichiometric VC, V_8C_7, and V_4C_3. The appearance of two additional peaks in the region of minimum DOS is clearly seen. These peaks are broadened and shifted upwards in energy with increasing vacancy concentration. The Fermi level moves downwards, in accordance with experimental observations.[15,38]

Our set of periodic structures allowed for an analysis of ECI's for clusters within the third-nearest-neighbor distance. Using the criteria described in Sec. II, we found that a set of eight cluster functions (cf. Table II) minimizes the weighted variance of Eq. (4). These ECI's reproduce the total energies of our periodic structures within a root-mean-square (rms) error of 0.6 mRy/atom. The largest contribution to the rms error came from a shift in the total energy of approximately 2 mRy between the two sets of calculations using different NaCl superstructure unit cells. If we corrected for this discrepancy, the agreement was essentially perfect. The value of the orthogonality parameter $\mathcal{O}$ from Eq. (6) was 0.25. Although the second-, third- and fourth-nearest-neighbor pair interactions in certain studies[19,25] have been found

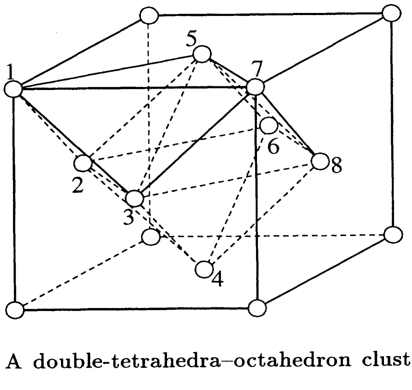

FIG. 1. A double-tetrahedra–octahedron cluster for a fcc lattice.

TABLE I. Calculated enthalpies of formation, bulk moduli, and equilibrium lattice constants. The unit cell of the six monoclinic structures is the double-tetrahedra–octahedron cluster of the carbon fcc sublattice (cf. Fig. 1) with C atoms removed from the indicated vertices.

Composition	Structure	$-\Delta^0 H$ (mRy/V atom)	B (Mbar)	a_0 (a.u.)
V	fcc		1.96	7.07
V_4C	sc	43.1	1.96	7.16
V_2C	$L1_1$	66.3	2.12	7.37
V_4C_3	sc	83.0	2.56	7.51
V_8C_7	monoclinic (2)	105.8	2.71	7.55
V_4C_3	monoclinic (2,3)	100.0	2.64	7.49
V_4C_3	monoclinic (2,8)	93.5	2.66	7.50
V_4C_3	monoclinic (2,7)	103.9	2.62	7.48
V_8C_5	monoclinic (1,2,3)	94.0	2.45	7.41
V_8C_5	monoclinic (1,2,7)	80.0	2.48	7.44
VC	fcc	106.7	2.95	7.62
C	hexagonal			4.62

to be equally important, we note in this case that the extracted fourth-nearest-neighbor pair ECI is approximately 1 mRy and does not improve the convergence of the cluster expansion. Furthermore, we estimate that the most important ECI excluded from our set is the one corresponding to a linear square formed by nearest neighbors.

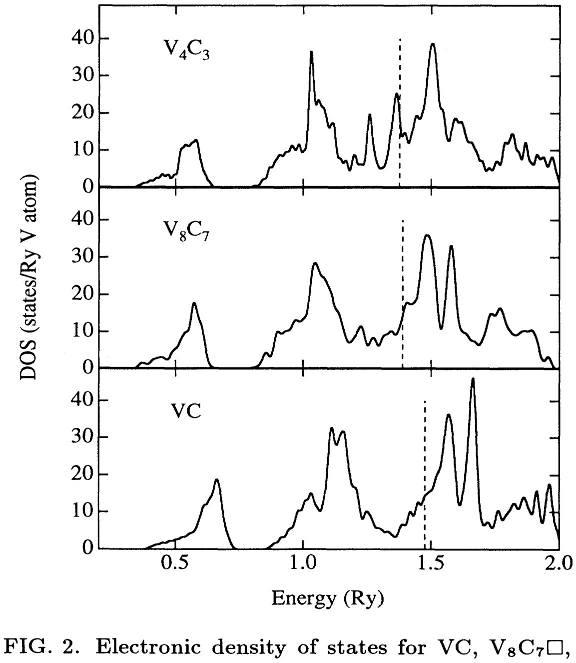

FIG. 2. Electronic density of states for VC, $V_8C_7\square$, and $V_4C_3\square$.

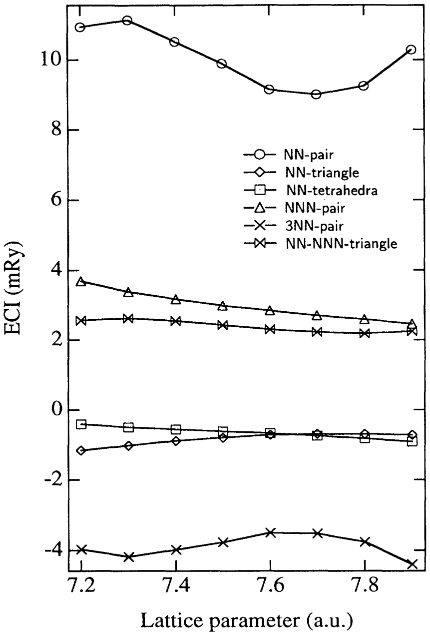

FIG. 3. Effective cluster interactions for VC_{1-x} as functions of the lattice parameter. See also Table II.

The volume dependence of the calculated ECI's is shown in Fig. 3. The ECI's corresponding to nearest-neighbor (NN) and next-nearest-neighbor (NNN) pairs are both large and positive. However, the NNN-pair interaction is smaller than one-half of the NN-pair ECI. Thus, for a model with only NN-pair and NNN-pair interactions, our values predict that the V_6C_5 structure is unstable.[22,39–42] The ECI of the third-nearest-neighbor (3NN) pair is found to be large and negative. This agrees well with the experimental observation[43–45,48–50] that, in all ordered VC_{1-x} superstructures, vacancies tend to form 3NN pairs. The large positive NN-NNN-triplet ECI favors ordered superstructures formed by stacking partly vacant fcc (111) planes, since this cluster always contains sites from neighboring (111) planes. We finally note that our study gives equal total energies for all three V_6C_5 periodic structures (cf. Fig. 4) that have been proposed as the possible ground states of V_6C_5.[43–45] These structures have identical cluster correlation functions $\overline{\Phi}_\alpha$ for all clusters listed in Table II. This degeneracy can be lifted only by including much more distant interactions. For instance, the monoclinic "*B*" structure[43] and the hexagonal "*V*" structure[44] (cf. Fig. 4) differ in the 23rd nearest-neighbor pair correlation functions.[46] It is interesting to note that there is recent experimental evidence[47] from transmission electron microscopy studies suggesting that the monoclinic *B* cell of Billingham, Bell, and Lewis[43] is the preferred ground state of V_6C_5.

Using the cluster expansion of the total electronic energy [Eq. (3)], the total energy of any structure can be predicted. In particular, we have calculated the enthalpies of formation of two ordered compounds with composition V_8C_7 and V_6C_5. The unit cells of these compounds are shown in Fig. 4. In Fig. 5 we have marked two points corresponding to the enthalpies of formation of these ordered V_8C_7 and V_6C_5 compounds. We note that these substoichiometric compounds have *lower* enthalpies of formation than stoichiometric VC, i.e., they are energetically favorable. This conclusion is supported by the experimental observation that both ordered V_8C_7 and V_6C_5 are very easy to form below their order-disorder transition temperatures which are about 1395 K and 1435 K, respectively.[50]

In order to test the predictions of our ECI's for the energies of ordered structures which are not included in the set of Table I, we performed direct *ab initio* calculations for the V_6C_5 monoclinic G cell[45] in Fig. 4. Table III lists the enthalpies of formation obtained from *ab initio* calculations and those obtained from the cluster expansion in Eq. (3). We see that the results agree within 2 mRy/V atom.

The heat of formation $\Delta E^{\rm dis}(V,x)$ of a compound with a completely disordered vacancy configuration is obtained from Eq. (3) by setting $\overline{\Phi}_\alpha(\phi) = [(+1)(1-x) + (-1)x]^n = (1-2x)^n$, where n is the number of vertices in the cluster α. Figure 6 shows $\Delta E^{\rm dis}(V,x)$ for VC_{1-x} as a function of the lattice parameter and vacancy concentration. We note that, for small lattice parameters, the heat of formation reaches a maximum when $x \neq 0$. The enthalpy of formation $\Delta^0 H^{\rm dis}(x)$ of disordered VC_{1-x} is obtained by maximizing $\Delta E^{\rm dis}(V,x)$ with respect to the lattice parameter at fixed vacancy concentration x. The resulting curve in Fig. 5 shows that $\Delta^0 H^{\rm dis}(x)$ is a monotonously increasing function of vacancy concentration x. Hence, it is always energetically unfavorable to form disordered substoichiometric VC_{1-x} at 0 K. The ordering energy $\Delta E^{\rm ord}(x)$ can be defined as

$$\Delta E^{\rm ord}(x) = \Delta^0 H^{\rm ord}[VC_{1-x}] - \Delta^0 H^{\rm dis}(x). \qquad (9)$$

We obtain $\Delta E^{\rm ord}(1/8) = 8.6$ mRy/V atom and $\Delta E^{\rm ord}(1/6) = 15.3$ mRy/V atom, respectively, for the

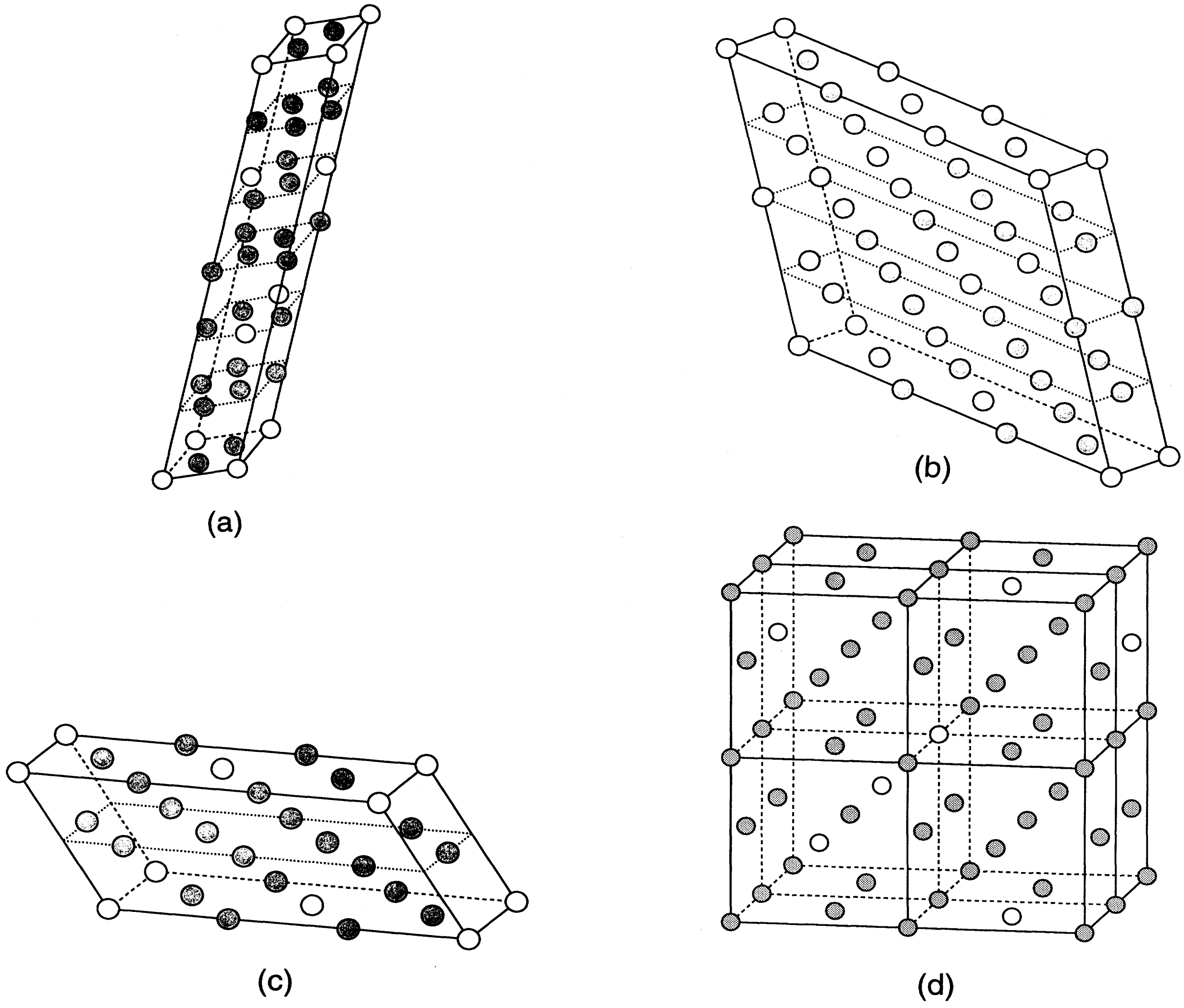

FIG. 4. Proposed ground-state crystal structures for $V_6C_5\square$ and $V_8C_7\square$ (V atoms have been omitted for clarity). Filled circles correspond to carbon atoms, fcc (111) planes have been marked with dotted lines. (a) V_6C_5 hexagonal V cell proposed by Venables, Kahn, and Lye (Ref. 44). (b) V_6C_5 monoclinic B cell proposed by Billingham, Bell, and Lewis (Ref. 43). (c) V_6C_5 monoclinic G cell proposed by Gusev and Rempel (Ref. 45). (d) The cubic conventional cell of V_8C_7 (Refs. 48–50).

TABLE II. Volume dependence of calculated effective cluster interactions for VC_{1-x}. The lattice parameters a are given in atomic units. m_α denotes the multiplicity of each cluster.

Cluster	m_α	$E_\alpha(V)$ (mRy)				
		$a = 7.3$ (a.u.)	$a = 7.4$ (a.u.)	$a = 7.5$ (a.u.)	$a = 7.6$ (a.u.)	$a = 7.7$ (a.u.)
empty	1	-66.55	-66.95	-64.70	-60.36	-53.67
point	1	-54.28	-62.15	-68.46	-73.31	-77.16
NN pair	6	11.15	10.53	9.90	9.15	9.00
NNN pair	3	3.38	3.16	2.98	2.84	2.69
3NN pair	12	-4.18	-3.98	-3.78	-3.50	-3.53
NN triangle	8	-1.02	-0.89	-0.80	-0.73	-0.69
NN-NNN triangle	6	2.62	2.54	2.42	2.29	2.22
NN tetrahedron	2	-0.50	-0.56	-0.62	-0.67	-0.75

ordered V_8C_7 and V_6C_5 compounds shown in Fig. 4.

The enthalpy of formation of disordered VC_{1-x} can be fitted to a series expansion in the powers of vacancy concentration x,

$$\Delta^0 H(x) = -105.8 + 28.5x + 104.2x^2 + 2.8x^3 - 31.6x^4 \quad [\text{mRy/V atom}]. \tag{10}$$

This expansion can be compared with results obtained using the empirical two-sublattice model for substitutional solutions.[33] The dashed curve in Fig. 5 is from an analysis of thermodynamic information on the vanadium-carbon system by Huang.[32] We note that there is a close agreement between the *trends* in theoretical and experimental results. The shift in $\Delta^0 H(x)$, which is present also for $x = 0$, can be largely attributed to the use of the LDA in the theoretical calculations.

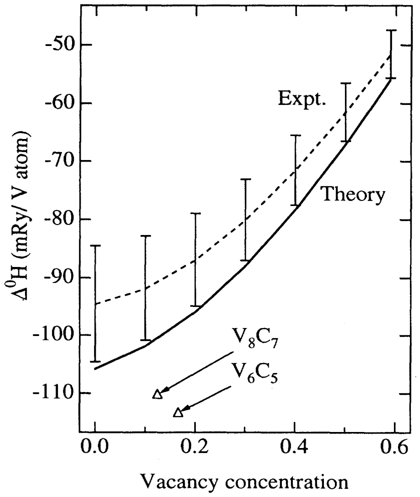

FIG. 5. Enthalpy of formation $\Delta^0 H^{\text{dis}}(x)$ of disordered VC_{1-x} vs vacancy concentration x. The experimental curve is from Huang (Ref. 32). Open triangles show $\Delta^0 H$ values for ordered V_8C_7 and V_6C_5.

TABLE III. Enthalpies of formation of V_6C_5 in the monoclinic "G" structure derived from direct calculations and from a cluster expansion [Eq. (3)].

Lattice parameter (a.u.)	$-\Delta^0 H$ calculated (mRy/V atom)	$-\Delta^0 H$ Eq. (3) (mRy/V atom)
7.50	111.4	113.3

V. DISCUSSION

A. ECI's and enthalpies of formation

Our ECI's in Table II support the prediction of the generalized perturbation method[19,20] (GPM) that the magnitude of multiplet ECI's of TM carbides decreases with an increased number of vertices in the cluster. The nearest-neighbor pair interaction for VC_{1-x} is by far the strongest, but the NNN pair and the third-nearest-neighbor pair interactions are equally important. This contradicts values of NN-pair and NNN-pair interactions obtained by fitting experimental data from elastic neutron diffuse scattering[17] or those calculated using the GPM.[19,20,22] However, a direct comparison is questionable since the interactions derived from the GPM or experimental data are concentration dependent, and our triplet interactions for VC_{1-x} are non-negligible.

Experimental x-ray and thermal neutron-scattering studies[51] have unambiguously proved that vanadium atoms in substoichiometric VC_{1-x} shift away from the vacant sites so that the bond length with nearest-neighbor carbon atoms is reduced by approximately 3%. Displacements of carbon atoms are typically much smaller[51] and directed towards the vacant site. In principle, one can account for these sublattice relaxations in a cluster expansion by performing calculations on relaxed structures.[25–27,29] It has been pointed out[27,29] that a larger number of ECI's must then be included and that

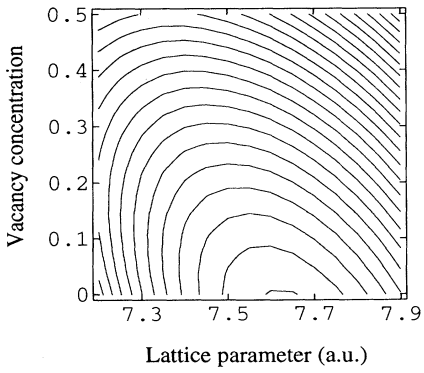

FIG. 6. Heat of formation $\Delta E^{\text{dis}}(V, x)$ of disordered VC_{1-x} vs the lattice parameter and concentration of vacancies. The energy difference between two consecutive levels is 3 mRy/V atom. $\Delta E^{\text{dis}}(V, x)$ reaches a global maximum when $x = 0$ and $a = 7.62$ a.u.

the convergence of the cluster expansion [Eq. (3)] may be considerably reduced. Thus, sublattice relaxations for complex systems are computationally very demanding, which is why they were not included in the present study. As local relaxations are neglected, we refrain from a calculation of order-disorder transition temperatures since these are sensitive to small differences in total energies. However, we note that our set of ECI's gives reliable predictions for the total energies of unrelaxed periodic structures. Since the sublattice relaxations can only *decrease* the total energy of VC_{1-x}, they will not change our main conclusion, i.e., that ordered V_8C_7 and V_6C_5 have lower enthalpies of formation than VC. Relaxations may influence the relative values of ECI's in Table II, e.g., the NNN pair ECI may be increased. It has been suggested[10,50,51] that energy gains due to displacements of vanadium atoms towards the neighboring carbon sites may be partly responsible for the fact that vacancies avoid to form NNN pairs on the carbon sublattice.

B. Electronic structure of substoichiometric TM carbides

Electronic states formed by the hybridization between carbon *p* and transition-metal *d* orbitals can be classified as bonding, nonbonding, and antibonding,[14] depending on their contributions to the enthalpy of formation. For instance, states whose occupation decreases the magnitude of the enthalpy of formation are called antibonding. In TM carbides, a minimum in the total DOS separates bonding from antibonding and nonbonding electronic states. The bonding states can accommodate six electrons, thus giving rise to a maximum stability of stoichiometric carbides of the group-IV transition metals, e.g., TiC. In VC, the Fermi level lies above the minimum DOS and some of the antibonding states are occupied. Thus, VC is expected to be chemically less stable than TiC.[11]

Several authors have pointed out that rigid band arguments cannot be applied indiscriminately to substoichiometric compounds.[3–5,12] Our results, presented in Sec. IV, confirm the appearance of new states in the region of minimum DOS. However, we believe that the trends in bonding energies can be still qualitatively understood using simple band-filling arguments. Removal of a carbon atom destroys two states from the C 2*s* band, three filled bonding and three antibonding *p*-*d* states, one of which is filled. *d* electrons from the surrounding octahedron of vanadium atoms will tend to form new *d*-*d* bonds of essentially metallic character. We interpret the so-called vacancy peaks to be precursors of the fcc vanadium DOS and, as such, they should be classified as nonbonding states. These nonbonding states will accommodate electrons from antibonding states, thus reducing the cost of breaking strong covalent *p*-*d* bonds. The Fermi energy of VC_{1-x} will decrease due to the occupation of these metal-like states. When all antibonding states are emptied, the vacancy formation energy will increase. This increased vacancy formation energy is clearly seen in both the theoretical and the experimental $\Delta^0 H(x)$ curves in Fig. 5.

VI. SUMMARY

From *ab initio* electronic band-structure calculations using a full-potential LMTO method,[30] we have determined a set of eight volume-dependent effective cluster interactions (ECI's) for VC_{1-x}. Pair interactions up to the third-nearest neighbors and several multiplet ECI's accurately describe the energetics of all ordered structures considered. We use the ECI's to predict the enthalpies of formation of ordered V_8C_7 and V_6C_5 compounds and of completely disordered VC_{1-x}. We find that it is energetically unfavorable to form disordered VC_{1-x} compounds at 0 K. However, the vacancy ordering energy is large (approximately 10 mRy/atom) and it makes formation of certain *ordered* substoichiometric VC_{1-x} compounds energetically favorable. Thus, our study explains why it is difficult to prepare stoichiometric VC at ambient pressure. We discuss the effects of vanadium sublattice relaxations around the vacant sites arguing that these will increase the stability of substoichiometric VC_{1-x} compounds. Further, our results are found to be in reasonable agreement with those of the empirical two-sublattice model.[31–33] Finally, we present a simple model which explains the limited range of vacancy formation in terms of band-filling arguments.

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