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Density functional theory study of ternary V-Cr-N compounds

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The *Z*-phase VCrN is important for steel technology because of its harmful influence on the mechanical properties of 9%–12% Cr steel with V additions. The thermodynamical stability of the *Z* phase and related ternary compounds with respect to the decomposition into binary Cr- and V-nitride phases is studied. By application of the density functional theory (DFT) approach we investigate the ground-state properties of a variety of binary V-N and Cr-N compounds, and we propose the existence of a different phase V_4N_5. Concerning ternary phases, we studied the compounds VCrN, $V_2Cr_2N_3$, and $VCrN_2$ for two structural variants, namely, for an alternating single-layer (V-N)/(Cr-N) [100] stacked rocksalt structure and for a double-layer (V-N V-N)/(Cr-N Cr-N) [100] stacked tetragonal structure. For the *Z*-phase VCrN, the tetragonal structure with pure Cr layers is most stable, whereas for the composition $VCrN_2$ both structural variants are almost degenerate. The intermediate phase $V_2Cr_2N_3$ is unstable against a decomposition into VCrN and $VCrN_2$. Comparing the formation energies of ternary and binary nitrides, we find that the *Z*-phase VCrN is always stable whereas $VCrN_2$ is less stable than a mixture of V_4N_5 and Cr_2N. Assuming nonequilibrium conditions for which nitrogen might be abundant, also the *Z*-phase VCrN can decompose into binary nitrides. Applying an empirical temperature-dependent approach to study the formation of nitrides of Cr and V dissolved in Fe, the DFT data are corroborated concerning the *Z*-phase VCrN and VN. For Cr_2N the empirical approach yields a formation energy which is about 20% more stable than the DFT data. The DFT data are, however, in good agreement with a corresponding measured value.

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I. INTRODUCTION

Recently, the so-called *Z* phase—an ordered compound of composition CrVN—has attracted considerable interest because its nucleation and growth seems to be responsible for rapid deteriorating of creep properties of steel containing 9%–12% Cr after long-term service exposure.[1] 9%–12% Cr steel are important materials in power plant application, where excellent creep resistance at elevated temperature is required. Their high strength and superior long-term creep resistance is mainly attributed to a fine-grained ferritic/martensitic microstructure, which is typical for tempered martensites, and a high density of precipitates, which very efficiently stabilize and preserve the initial microstructure over a long period of time. Typical precipitates in 9%–12% Cr steel are Cr-rich $M_{23}C_6$ (M=Fe, Cr) carbides, Laves phase particles, and fine and densely distributed vanadium nitrides, which in particular contribute to the mentioned high strength via precipitation hardening. In 9%–12% Cr steel with addition of vanadium and nitrogen, coarse-grained particles of the so-called *Z*-phase CrVN can be nucleating and growing at the expense of finely dispersed precipitates of vanadium nitride.[2] Dissolution of the vanadium nitrides leads to a detrimental decrease in the creep resistance of the microstructure, which makes the *Z* phase a harmful microstructural constituent.

For many years, the *Z* phase is known to precipitate in austenitic steel. In these materials, however, V is usually substituted by Nb.[3,4] More recently, a *Z* phase with composition $Cr_2(Nb,V)_2N_2$ has been identified in ferritic/martensitic steel after long-term thermal treatment at elevated temperatures between 550 °C and 650 °C.[5] In these steels, it has also been observed that the *Z* phase often forms in close vicinity to VN precipitates. In a recent study, the *Z* phase in ferritic/martensitic steel has been found to nucleate and grow directly on V nitrides by diffusion of Cr into already existing vanadium nitride precipitates.[6] Single *Z*-phase precipitates are able to dissolve a sizeable amount of vanadium nitrides by which process the important strengthening effect of the nitrides is destroyed.

In order to gain some insight into the phase stabilities of the nitride phases we calculate the formation energies of a variety of binary V-N and Cr-N compounds which are competing with the ternary *Z*-phase VCrN and its related nitrogen-rich variant $VCrN_2$, which we name as the filled *Z* phase. Both *Z* phases were studied as tetragonal structure as well as rocksalt structure because this cubic structure has been proposed recently.[6] In combination with density functional theory (DFT) results for the binary compounds, the stability of the *Z* phases under varying N content is investigated.

The calculations are done by an *ab initio* DFT approach, which provides reliable results being free from any empirical parameters. Also, the DFT data are compared to a recent thermodynamic analysis of the Gibbs energy of the *Z* phase[7] which is based on the computer coupling of phase diagrams and thermochemistry (CALPHAD) methodology,[8] as it is a well-established procedure in the material science community.

II. COMPUTATIONAL ASPECTS

The DFT (Refs. 9 and 10) calculations were performed by applying the Vienna *ab initio* simulation package (VASP)

TABLE I. DFT energies of formation ΔU_f (in kJ mol^{-1} atoms^{-1}) of various phases and crystal structures of V_mN_n and respective calculated lattice parameters a and c in Å (the corresponding experimental values in brackets are from Ref. 15). The cubic phases are variants of the rocksalt structure. The value for $\Delta U_{f,\mathrm{mix}} = 0.96\Delta U_f[V_7Vac(V)N_8]$ results from mixing the nitrogen-rich vacancy phase and pure N.

Phase	V_4N_5 Tetragonal	$V_7Vac(V)N_8$ Cubic	VN Cubic	$V_8N_7Vac(N)$ Cubic	V_2N Hexagonal
ΔU_f	−98.0	−99.5	−98.5	−100.5	−97.3
$\Delta U_{f,\mathrm{mix}}$	−95.3				
a	4.02	4.09	4.13	4.10	4.89
			[4.14]	[4.10]	[4.46]
c	6.40				4.53
					[4.67]

which makes use of the projector augmented wave (PAW) construction for the pseudopotential.[11,12] The generalized gradient approximation of Perdew and Wang[13] was chosen for parametrizing the exchange-correlation functional. Equilibrium volumes and cell shapes (i.e., the crystallographic structures) of the calculated compounds were optimized by minimizing the stress tensor components. Internal structural parameters are relaxed by minimizing the forces acting on the atoms within a conjugate-gradient algorithm. Therefore, all DFT data refer to systems with fully relaxed geometrical degrees of freedom, i.e., for the ground states of each considered compound. For the *ab initio* part of study no empirical materials parameters were introduced.

For the specific compound $V_aCr_bN_c$ with $a,\ b,\ c$ numbers of V, Cr, and N atoms in the unit cell, the energy of formation ΔU_f is defined by the difference of corresponding DFT total energies U_{DFT} according to

$$\Delta U_f = \frac{1}{a+b+c} \times \Big\{ U_{\mathrm{DFT}}(V_aCr_bN_c) - aU_{\mathrm{DFT}}(V) - bU_{\mathrm{DFT}}(Cr) - c\frac{1}{2}U_{\mathrm{DFT}}(N_2) \Big\}. \quad (1)$$

All formation energies of our studies are given in units of kJ mol^{-1} atoms^{-1}. The reference energies for the pure states were calculated for the solid phases of bcc V and bcc antiferromagnetic Cr and for the N_2 molecule. Our DFT results—as for all standard DFT approaches—are strictly valid only at $T=0$ K or sufficiently low temperatures. For most cases internal energies such as ΔU_f are, however, rather insensitive to temperature. DFT studies can be extended to temperature-dependent free energies by including DFT derived results for the vibrational free energy.[14] Such investigations are much more elaborate and go beyond the scope of the present study. For modeling vacancies in the rocksalt structure, supercells were constructed with 64 atomic sites in total with up to six vacancies on each sublattice. The local quantities such as local magnetic moments were calculated within spheres of radii of 1.323 Å for V and 1.217 for Cr.

A. Results and discussion

1. Binary V-N compounds

The most common V-N compounds crystallize in the rocksalt structure. Because the compounds $V_{1-x}N_x$ with $x \approx 0.5$ are prone to formation of vacancies on both sublattices, we performed DFT calculations for a larger variety of compositions including vacancies in the sublattices. Table I only shows the results for the most stable phases. Averaging the formation energies for V_7N_8 (−99.5 kJ mol^{-1} atoms^{-1}) and for V_8N_7 (−100.5 kJ mol^{-1} atoms^{-1}) yields a value of −100 kJ mol^{-1} atoms^{-1}, which is lower than the formation energy of −98.5 kJ mol^{-1} atoms^{-1} for the perfectly stoichiometric compound VN, which is therefore unstable against a mixture of vacancy phases. Other intrinsic defects such as antisite defects can be excluded because calculations with antisite defects (in which V resides on a site of the N sublattice, and vice versa) result in very unfavorable formation energies. The tendency of vacancy formation for the vanadium nitrides is very well known from experiment.[16–18] Furthermore, it was observed that stoichiometric VN samples ($V_{1-x}N_x$ of $x \approx 0.5$) distort into a tetragonal structure at low temperatures.[19] Very recent DFT calculations revealed that epitaxially strained VN transforms into a modified rocksalt-type structure[20] which verifies an instability with respect to a tetragonal distortion.

According to the phase diagram,[21] an ordered phase V_2N is stable at vanadium-rich conditions and it crystallizes in the hexagonal close-packed ϵ-Fe_2N-type structure. Our DFT results for the ground-state structure for this phase are in good agreement with experiment; e.g., DFT volume of 93.9 Å^3 is only 1.8 % smaller than the experimental value.[22]

Discussing nitrogen-richer compounds, for tantalum nitrides an ordered phase Ta_4N_5 (Ref. 23) appears, which crystallizes in a variant of the rocksalt structure in space group $I4/m$. Remarkably, this compound contains an ordered arrangement of vacancies on the Ta sublattice. On the other hand, a V_4N_5 compound has not been found yet. Performing DFT calculations for V_4N_5 with the structure of Ta_4N_5 we predict the existence of this vanadium compound because—applying our results in Table I—its energy of formation of −98 kJ mol^{-1} atoms^{-1} is more negative than a phase consisting of suitable mixture of V_7N_8 and pure N which results in −95.3 kJ mol^{-1} atoms^{-1}. Since no other nitrogen-richer phase is known up to now V_4N_5 should be stable at least at low temperatures.

The energies of formation for the discussed $V_{1-x}N_x$ phases are very similar to each other resulting in a rather straight ground-state line in the phase diagram in a range of

TABLE II. DFT-derived energies of formation (in kJ mol^{-1} atoms^{-1}) of Cr_mN_n phases and respective calculated lattice parameters a and c in Å (the corresponding experimental values in brackets are taken from Ref. 15). The cubic phases are variants of the rocksalt structure. The value of $\Delta U_{f,\text{mix}}$ results from the mixture of formation energies of CrN and Cr_2N; $\frac{1}{7}(4\Delta U_f[\text{CrN}] + 3\Delta U_f[Cr_2N])$.

Phase	CrN Cubic	$Cr_4Vac(N)N_3$ Cubic	Cr_2N Hexagonal
ΔU_f	−38.7	−33.0	−40.5
$\Delta U_{f,\text{mix}}$		−39.5	
a	4.13	4.01	2.76
	[4.14]		[2.75]
c			4.40
			[4.46]

≈25 at. % for $0.4 < x < 0.65$. Therefore, a variety of phases with different (vacancy) structures might compete with each other as known from experiment.[16] In other words, the formation energy of stable V-N compounds is rather independent of the nitrogen concentration.

2. Binary Cr-N compounds

In comparison with the V-N compounds the energies of formation for the binary Cr-N compounds (Table II) indicate a significantly weaker bonding because ΔU_f for Cr_2N and CrN is less negative by a factor of about 2.5.

According to our DFT calculation CrN is antiferromagnetic with local magnetic moments of $\pm 2.2\mu_B$ for Cr, whereas for Cr_2N no magnetic ordering was found. The Cr-N phases are much less prone to form vacancies in strong distinction to VN: the energy $\Delta U_f = -33.0$ kJ mol^{-1} atoms^{-1} for an ordered vacancy phase Cr_4N_3 (as modeled by a rocksalt structure with one vacancy on the N sublattice) is less negative by 6.5 kJ mol^{-1} atoms^{-1} than a suitable linear combination of energies of the neighboring phases CrN and Cr_2N (see Table II). These findings of structural stability are in excellent agreement with data reported in the literature. According to x-ray diffraction data,[18] a cubic CrN_y phase containing nitrogen vacancies exists only for a narrow range of nonstoichiometry of $(0.9 < y < 1)$. There, it is also reported that CrN_y films with nominal compositions of $0.5 < y < 0.9$ do not crystallize in a single cubic phase because of a phase mixture of cubic CrN and hexagonal Cr_2N.

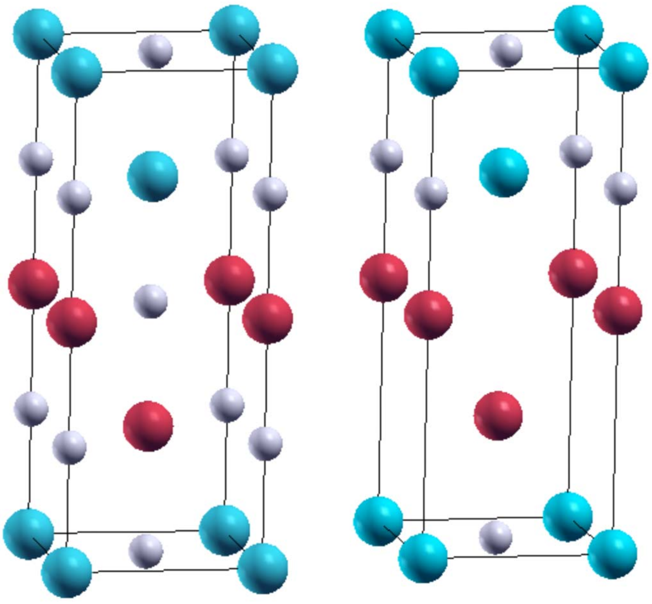

FIG. 1. (Color online) Tetragonal structure of the filled *Z*-phase $VCrN_2$ [panel (a)] and the *Z*-phase VCrN with pure Cr layers [panel (b)]. Red spheres: Cr; blue spheres: V; and gray small spheres: N.

3. Ternary V-Cr-N compounds

Table III summarizes the DFT data for a variety of ternary V-Cr-N compounds, which we studied within the body-centered tetragonal (bct) structure, as well as for some related rocksalt structural variants. The bct structure—originally proposed by Jack[4] for NbCrN—was suggested for the *Z*-phase VCrN by Strang and Vodarek.[5] This structure [Fig. 1, panel (b)] can be constructed out of a rocksalt supercell structure [Fig. 1, panel (a)] for which in [100] direction double layers of V-N and Cr-N are stacked and the N atoms are removed from the Cr-N layers. According to Table III the bct lattice parameters of $a = 2.86$ Å, $c = 7.14$ Å, and $c/a = 2.502$ are in good agreement to the structural data of Ref. 5 ($a = 2.86$ Å and $c = 7.39$ Å) and formation energy of −75.1 kJ mol^{-1} atoms^{-1} indicates strong bonding. The *Z* phase is nonmagnetic because no local magnetic moments

TABLE III. DFT lattice parameters a_{tet}, a_{cub}, and c (in Å), atomic volume V (in Å^3), bulk modulus B_0 (in GPa), and energy of formation ΔU_f (in kJ mol^{-1} atoms^{-1}) for ternary V-Cr-N compounds in *Z*-phaselike structures and related rocksalt variants. FI is ferrimagnetic spin ordering; see text.

	Phase	$a_{\text{tet}}/a_{\text{cub}}$	c	V	B_0	ΔU_f
Z	VCrN	2.86	7.14	58.40	309	−75.1
Z-phaselike	$V_2Cr_2N_3$	2.88	7.84	65.03		−68.7
Z-filled	$VCrN_2$ (FI)	2.90	8.34	70.14	269	−68.3
Rocksalt	VCrN	3.991	3.867	61.6	274	−59.2
Rocksalt	$V_2Cr_2N_3$	4.033	4.025	65.47	266	−66.1
Rocksalt	$VCrN_2$ (FI)	4.134	4.125	70.50	261	−68.5

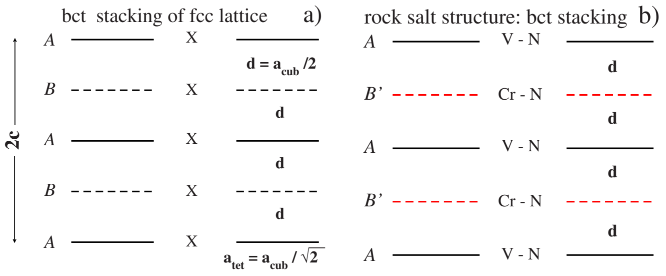

FIG. 2. (Color online) Panel (a): sketch of a bct lattice corresponding to an fcc lattice for four X atoms. The parameter a_{cub} is the lattice parameter for a cubic unit cell, whereas the basal tetragonal parameter is $a_{\mathrm{tet}}=a_{\mathrm{cub}}/\sqrt{2}$. Panel (b): sketch of a variant of the rocksalt structure in bct stacking for VCrN_2. Unprimed stacking labels A, B refer to X atoms or V-N layers, whereas the primed label B' marks Cr-N layers. d is the layer distance.

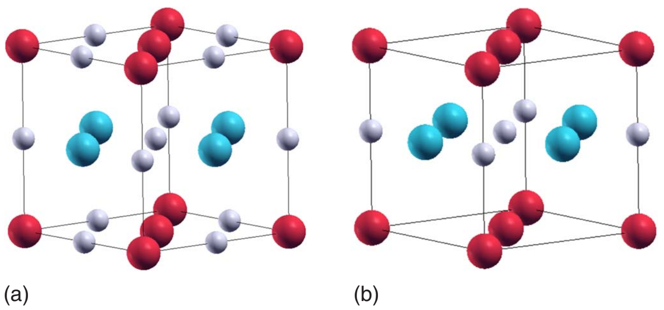

FIG. 4. (Color online) Rocksalt variant of VCrN_2 [panel (a)] and VCrN with pure Cr layers [panel (b)]. Red spheres: Cr; blue spheres: V; and gray small spheres: N. Note that both structures are tetragonal because of different stackings in the cubic main directions.

could be stabilized by a spin-polarized calculation.

A Z-phase compound VCrN with pure V and Cr-N layers [i.e., exchanging V and Cr in Fig. 1(a)] is energetically very unfavorable because of its $\Delta U_f=-39.1$ kJ mol^{-1} atoms^{-1}, which is almost a factor of 2 less bonding than for the original Z phase. This indicates that the nearest-neighbor bonding between V-N atoms is very important for the stability of V-Cr-N compounds.

Inspecting Fig. 2(a), one realizes the ideal ratio of $c/a_{\mathrm{tet}}=2\sqrt{2}=2.83$. However, the DFT result for the Z phase (see Table III) is $c/a_{\mathrm{tet}}=2.50$ revealing a strong compression along the tetragonal axis. The basal lattice parameter $a_{\mathrm{cub}}=2.86\sqrt{2}=4.04$, however, is rather close to the DFT-derived cubic lattice parameter $a_{\mathrm{cub}}=4.13$ Å of VN.[20]

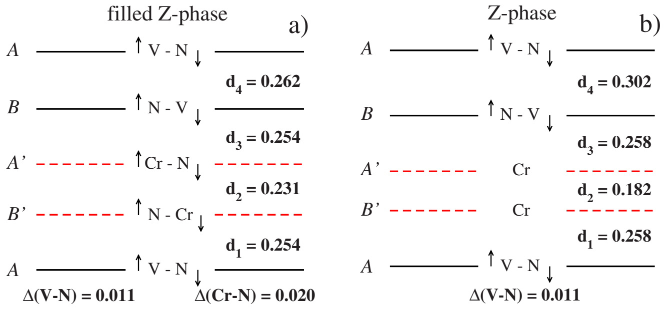

FIG. 3. (Color online) Layer stacking along the c axis for the Z phase for the filled structure [panel (a)] and a structure without N atoms in the Cr layers [panel (b)] [according to Fig. 1(a)]. Unprimed stacking labels A, B refer to V-N layers and primed labels A', B' mark Cr-N layers. Layer distances and layer rumplings Δ are given in units of the c axis. The rumpling (i.e., shift of atoms relative to the central layer position) is indicated by arrows on each atomic species.

Figure 3 sketches the layer distances d for the Z-phase VCrN and its filled variant VCrN_2. Taking the equidistant layer spacing of $d=0.25$ as a reference, the nitrogen-free Cr layers move strongly together by 27% widening the distances between the double V-N layers by 21%. The distance between the V-N and Cr layers, however, remains close to the ideal value. The so-called filled Z-phase VCrN_2 [see Figs. 1(a) and 3(a)] is constructed by filling up the pure Cr layers of the Z phase [see Figs. 1(b) and 3(b)] by N atoms. For VCrN_2 the values for the lattice parameters in Table III yield an almost ideal cubic ratio of $c/a=2.88$. Consequently, the layer distances are rather uniform [according to Fig. 3(a)] and change much less than for the Z-phase VCrN. The Cr-N layer distance is now shortened by only 8%. The geometrical rumpling in the two Cr-N layers is enhanced compared to the rumpling of V-N layers, which is the same as for the nitrogen deficient Z phase. Studying magnetic properties by spin-polarized calculations, it appeared that VCrN_2 is ferrimagnetic; i.e., the local magnetic moments on Cr and V atoms are oriented in opposite directions. Cr atom has a local moment of $1.94\mu_B$; while V atom has an antiparallel moment of $-0.52\mu_B$. The total magnetic moment per formula unit amounts to $1.42\mu_B$.

By filling N into just one of the pure Cr layers of the Z phase, the Z-phaselike compound $\mathrm{V}_2\mathrm{Cr}_2\mathrm{N}_3$ is buildup. (A similar phase with the same composition but with one pure V layer: one V-N and two Cr-N layers are energetically less favorable and therefore not considered) The DFT-derived lattice parameters of $a=2.88$ Å, $c=7.84$ Å, and $c/a=2.71$ are also in reasonable agreement with the structural model of Strang and Vodarek[5] ($a=2.86$ Å and $c=7.39$ Å). The comparison with the value of $c/a=2.50$ and the lattice parameter $a=2.86$ Å of the Z-phase VCrN reveals that the tetragonal parameter c is very sensitive to the amount of N in the compound. However, the Z-type phase $\mathrm{V}_2\mathrm{Cr}_2\mathrm{N}_3$ is thermodynamically unstable because a suitable mixture of the Z-phase VCrN and the filled rocksalt structure variant VCrN_2 (see Table III) is more stable by -2.6 kJ mol^{-1} atoms^{-1} than $\Delta U_f=-68.7$ kJ mol^{-1} atoms^{-1} for $\mathrm{V}_2\mathrm{Cr}_2\mathrm{N}_3$.

Recently, a cubic fcc-type crystal structure was proposed for VCrN particles[6] with a lattice parameter of 4.05 Å. We modeled this phase by constructing a suitable supercell based on the rocksalt structure in which V and Cr occupy one fcc sublattice, and N atoms occupy half of the available octahedral sites of the second fcc sublattice. By this procedure, a compound $\mathrm{Cr}_2\mathrm{V}_2\mathrm{N}_2$ (with the chemical formula unit VCrN) can be constructed in accordance with Ref. 6. Its structure is sketched in Fig. 4(b). It should be noted that both structures shown in Fig. 4 are tetragonal in general because the stacking along one of the cubic main directions (perpendicular to the Cr-N and V-N planes for the filled case and perpendicular to Cr and V-N layers for the *Z* phase) is different to the stacking in the remaining two directions, which involve mixed VCr-N planes. However, according to our DFT calculations the structure turned out to be almost cubic with a c/a ratio which is very close to one. This variant of the rocksalt structure may be viewed in terms of a tetragonal *Z* phase as sketched in Fig. 2(b). That reveals a very close relationship to the structure of the *Z* phases in Figs. 1 and 3: Viewing the stacking along the *c* axis for the rocksalt variant, one V-N layer alternates with one Cr-N layer, whereas for the *Z*-phase structure there are always double layers of V-N alternating with double layers of Cr-N (filled *Z* phase) or Cr (*Z* phase) layers. Therefore, we could define the rocksalt variant to be a single-layer stacked structure and the *Z* phase to be a double-layer stacked structure along the tetragonal axis.

For the rocksalt variants of VCrN vacancy structures can be constructed either by pure V layers, pure Cr layers, or a mixed configuration with N vacancies in each of the two (V,Cr)-N layers [in Fig. 4 compare panel (a) with panel (b)]. The compound with the pure Cr layers is actually the *Z* phase. The energies of formation are -53.1 kJ mol^{-1} atoms^{-1} for the mixed configuration, -59.2 kJ mol^{-1} atoms^{-1} for the structure with pure Cr layers, and -47.9 kJ mol^{-1} atoms^{-1} for the pure V layer case. Although the rocksalt variant with pure Cr layers is the lowest in energy, the bonding properties must be very different from the actual *Z* phase: whereas for the *Z* phase, the energy difference between the cases with pure V and pure Cr layers is 36 kJ mol^{-1} atoms^{-1} (referring to Table III and the discussion about the *Z* phase above), for the rocksalt variant it is much smaller, namely, only 9.4 kJ mol^{-1} atoms^{-1}. These findings seem to reflect the property of the binary V-N compounds for which the formation of vacancies on the N sublattice is energetically favorable.

The significantly less negative value of ΔU_f for the rocksalt variant of VCrN compared to the *Z* phase (the difference is 15.9 kJ mol^{-1} atoms^{-1}) indicates substantially weaker bonding. Consequently, rocksalt VCrN will not form under thermodynamical equilibrium conditions. Furthermore, its calculated equilibrium lattice parameters of $a=3.99$ Å and $c=3.87$ Å are significantly different from the claimed experimental value of 4.05 Å.[6] For the rocksalt variant VCrN, no magnetic ordering was builtup during the calculations.

As claimed in Ref. 6, in which a cubic *Z* phase is reported, it was not possible to measure the content of nitrogen. Therefore, it is possible that nitrogen atoms may also occupy more than half of the available octahedral sites of the second fcc sublattice. Therefore, two other rocksalt variants with compositions $V_2Cr_2N_3$ and $VCrN_2$ were constructed by gradually filling the vacancies of VCrN with nitrogen atoms until all sublattice sites were occupied. For $V_2Cr_2N_3$, there are two possible vacancy configurations (either in the V-N or the Cr-N layer) resulting in the DFT energies of formation of -58.7 and -66.1 kJ mol^{-1} atoms^{-1}. The most stable value (as also listed in Table III) refers to the case in which nitrogen vacancies are created in the Cr-N layer. According to Table III, comparing ΔU_f of the *Z*-phase-like compounds VCrN and $VCrN_2$ to their rocksalt variants, it is observed that for the rocksalt variant increasing the concentration of N decreases their formation energies, whereas for the double-layer stacked *Z*-type phases the trend is reversed. This is important for the discussion of structural stability versus N concentration (see Sec. II A 4).

Increasing the nitrogen concentration up to $VCrN_2$, the rocksalt variant becomes now stable according to $\Delta U_f = -68.5$ kJ mol^{-1} atoms^{-1}, but it is almost degenerate in energy with the filled *Z* phase having a value of $\Delta U_f = -68.3$ kJ mol^{-1} atoms^{-1}. This degeneracy of energies of formation means that phases $VCrN_2$ with stackings of single and double layers of (Cr,V)-N layers are equally stable and—as a speculation—maybe also stackings with triple or higher number of layers are thermodynamically possible. The energy of formation of the cubic compound $V_2Cr_2N_3$ is less negative than for its *Z*-phaselike counterpart by 2.7 kJ mol^{-1} atoms^{-1}.

Magnetic ordering is of significance for the bonding as can be estimated by comparing the ferrimagnetic DFT energy to a nonspin polarized calculations: the gain in magnetic energy is about -6 kJ mol^{-1} atoms^{-1}. The magnetic ordering and the size of the local moments are very close to the tetragonal *Z* phase. For the rocksalt variant the local Cr moment is $2.11\mu_B$ which is about four times larger than the antiparallel V moment of $-0.51\mu_B$. The total magnetic moment per formula unit is $1.6\mu_B$. Now, the Cr moment is about 10% larger than for the *Z* phase. Also the nitrogen-poorer rocksalt phase $V_2Cr_2N_3$ orders ferrimagnetically but with smaller local moments resulting in a total moment of $1.36\mu_B$ per formula unit.

From Table III one realizes that the lattice parameter of rocksalt $V_2Cr_2N_3$ of 4.03 Å compares very well with the experimental value of 4.05 Å. In addition, this phase has a very small lattice mismatch with respect to bcc Fe (or the steel matrix): from the DFT value for Fe $a_{\text{bcc}}(\text{Fe})=2.83$ Å the cubic lattice parameter $\sqrt{2}a_{\text{bcc}}(\text{Fe})=4.01$ Å is derived, which is only 0.5% smaller than the parameter for $V_2Cr_2N_3$. The chemical interaction with the Fe matrix may therefore aid to stabilize the $V_2Cr_2N_3$ phase.

Table III presents also values for elastic properties. The *Z* phase has the largest bulk modulus of 309 GPa, whereas $VCrN_2$ has a significantly lower values of 261 GPa in the single-stacked rocksalt variant and 269 GPa in the double-stacked *Z*-phaselike variant.

4. Thermodynamical stability of V-Cr-N compounds versus binary nitrides

The aim of our paper is the study of thermodynamical stability of the *Z*-phase VCrN and related nitrogen-richer ternary phases with respect to a decomposition into binary nitrides. When comparing the energy of formations per atom of phases *A* and *B* it should be noted that the number of atoms must be equal for both phases. Obeying this condition and applying the results of Tables I–III the stabilization energies $\Delta_{\text{ph}} = \Delta U_f[A] - \Delta U_f[B]$ are derived, as listed in Table IV. Negative (positive) values of Δ_{ph} indicate that phase $B(A)$ is stable.

Table IV is divided into two parts: Partition "equilibrium" compares equilibrium ground-state phases, whereas in partition "nonequilibrium" some redundant nitrogen remains unbound. The latter case might occur if redundant nitrogen dif-

TABLE IV. Relative stability of phase *A* vs *B*; $\Delta_{ph}=\Delta U_f(A)-\Delta U_f(B)$ as derived from the formation energies ΔU_f according to Tables I–III. A negative (positive) value of Δ_{ph} indicates that phase *B*(*A*) is stable. The arrow is pointing to the stable phase. Notation: Energy ΔU_f for the compound $V_aCr_bN_c$ is denoted as $[V_aCr_bN_c]$, and reference energies (which are all zero by definition) of the pure solid phases as [V] and [C], whereas [N] stands for the reference energy of the gaseous phase $1/2N_2$. All energies are given in units of kJ mol^{-1} $atoms^{-1}$. Partition "equilibrium" compares ground-state energies, whereas in partition "nonequilibrium" it is assumed that in-phase *B* redundant nitrogen is consumed by an external absorbing system.

Phase *A*		Phase *B*	Δ_{ph}
	Equilibrium		
$\frac{1}{16}(9[V_4N_5]+4[Cr]+3[N])$	→	$[VCrN_2]$	
-55.1		-68.5	-13.4
$\frac{1}{4}3[VCrN]+[N]$	→	$[VCrN_2]$	
-56.3		-68.5	-12.2
$\frac{1}{32}(15[V_8N_7]+12[Cr_2N]+5[N])$	→	$[VCrN_2]$	
-62.3		-68.5	-6.2
$\frac{1}{8}(3[Cr_2N]+4[VN])$	→	$[VCrN_2]$	
-64.4		-68.5	-4.1
$\frac{1}{2}([CrN]+[VN])$	→	$[VCrN_2]$	
-68.6		-68.5	0.1
$\frac{1}{16}(6[Cr_2N]+9[V_4N_5]+[N])$	←	$[VCrN_2]$	
-70.3		-68.5	1.8
-73.6		-71.3	2.3
$\frac{1}{3}(2[VN]+[Cr])$	→	$[VCrN]$	
-65.7		-75.1	-9.4
$\frac{1}{2}([Cr_2N]+[V_2N])$	→	$[VCrN]$	
-68.9		-75.1	-6.2
	Nonequilibrium		
$\frac{1}{16}(9[V_4N_5+4[Cr]+3[N]\ )$	→	$\frac{1}{4}(3[VCrN]+[N])$	
-55.1		-56.3	-1.2
$\frac{1}{27}(15[V_8N_7+12[Cr_2N])$	←	$\frac{1}{27}(24[VCrN]+3[N])$	
-73.8		-66.8	7.0
$\frac{1}{2}([CrN]+[VN])$	←	$\frac{1}{4}(3[VCrN]+[N])$	
-68.6		-56.3	9.3

fuses sufficiently fast away, e.g., to grain boundaries, the steel matrix, and so on, and does not participate in the formation of ternary compounds.

As shown by Table IV the relative stability of the nitrogen-rich phase $VCrN_2$ (the rocksalt variant is slightly more stable than the filled *Z* phase) is particularly strong when only no formation of chromium nitrides is taken into account. However, the separation of $VCrN_2$ into the stoichiometric binary compounds VN and CrN is possible as indicated by the stabilization energy of -0.1 kJ mol^{-1} $atoms^{-1}$. An even stronger tendency for the decomposition of $VCrN_2$ is observed when the mixture of V_4N_5 (the proposed V-N phase) and Cr_2N is considered. Therefore, in thermodynamical equilibrium at higher N concentrations the filled *Z* phase does not exist.

Reducing the amount of nitrogen for the formation of $V_2Cr_2N_3$ we found (as discussed in Sec. II A 3) that this ternary phase decomposes into VCrN and $VCrN_2$ and therefore it is not considered further on. For an atomic concentration of N of $x=3/7$, when a mixture of Cr_2N and VN is compared to a mixture of VCrN and $VCrN_2$, it turns out that the decomposition into binary compounds is more favorable by -2.3 kJ mol^{-1} $atoms^{-1}$.

Considering the nitrogen-poorest "equilibrium" cases (for $x=1/3$), the tetragonal *Z* phase shows a strong tendency to form. We could not find any combination of binary phases, which would be more stable than the *Z* phase. A variety of such combinations is given in Table IV.

The phase stabilities become different for the "nonequilibrium" case because it is possible to find phase mixtures which would lead to a decomposition of the tetragonal *Z*-phase VCrN provided that the abundant nitrogen is not bound and does not form nitrides with chromium and/or vanadium and is absorbed outside the considered thermodynamic system. If such nitrogen "absorbers" play a role, the formation of the *Z* phase would become much less probable.

Summarizing, at higher nitrogen concentrations it might happen that the harmful *Z*-phase VCrN decomposes into binary Cr and V nitrides.

5. Formation of Z phase in iron: an empirical estimation

The thermodynamics of the *Z* phase has recently been studied[7] in the framework of the CALPHAD approach.[8] With this method, the Gibbs energy of general multicomponent phases is described as a superposition of the Gibbs energies of the pure components, the ideal configurational entropy, magnetic contributions, and the excess Gibbs energy relating to all other energy contributions in excess to an ideal solution behavior. The parameters defining the Gibbs energy of the *Z* phase have been fitted on experimental data on *Z*-phase equilibria in several different ferritic and austenitic heat resistant steels (see Refs. 7 and 24).

Based on this thermodynamic assessment, the energies of formation have been calculated using the software MATCALC (Ref. 25) version 5.22. A chemical composition of 12 Cr, 0.05 N, 0.2 V (in mass %), and Fe (balance) has been assumed, which corresponds to typical alloying contents in ferritic martensitic heat resistant steel.

For the range of temperatures (approx. 500 °C to 850 °C) and chemical compositions where the CALPHAD thermodynamic assessment has been performed, the enthalpy of formation of *Z* phase is found to adopt values between -78 and -79 kJ mol^{-1} $atoms^{-1}$. The enthalpy of formation is evaluated as the change in system enthalpy on formation of an infinitesimally small amount of precipitate phase from the elements in solid solution with respect to one mole of atoms of the new phase. The values obtained from this calculus compare well with the present DFT value of -75.1 kJ mol^{-1} $atoms^{-1}$. Similar good agreement between CALPHAD and DFT values is obtained for the VN phase, where the CALPHAD values range between -94 and

$-98\ \mathrm{kJ\ mol^{-1}\ atoms^{-1}}$ compared to the DFT value of around $-100\ \mathrm{kJ\ mol^{-1}\ atoms^{-1}}$.

This good agreement is interesting because the two approaches use different reference states for calculation of the enthalpies of formation. The DFT simulation takes the pure elements as a starting configuration and evaluates the difference to the energy of the compounds. In the present CALPHAD simulations, a solid solution of V, Cr, and N in bcc Fe is taken as the reference state, and the difference to the precipitated state with the compound formed within the Fe matrix is evaluated. For comparison of the present DFT values with other methods, this different way of calculation is unfortunately unavoidable due to limitations in the validity of the CALPHAD thermodynamic database and the assessment of *Z* phase and VN. As a consequence of this limitation, it is also observed that the agreement in enthalpies of formation becomes worse in a temperature range where limited or no experimental information has been available in the CALPHAD thermodynamic assessment. At temperatures below 500 °C and above 900 °C, larger deviations between CALPHAD and DFT data are found. These uncertainties of an empirical approach emphasize the importance of a DFT approach, which provides the energetics of a solid compound studied under well-defined conditions without any empirical parameter involved.

Also, less good agreement is found for the enthalpy of formation of the Cr_2N compound, where the CALPHAD values vary between -53 and $-57\ \mathrm{kJ\ mol^{-1}\ atoms^{-1}}$ compared to a value of $-40.5\ \mathrm{kJ\ mol^{-1}\ atoms^{-1}}$ from the present DFT simulations. Again, this disagreement can be attributed to deficiencies of the CALPHAD data in this range of temperatures and compositions. Experimental evidence exists supporting the DFT values because the heat of formation of Cr_2N was measured to be $-42.8\ \mathrm{kJ\ mol^{-1}\ atoms^{-1}}$ at 298 K (Ref. 26) being in a good agreement with our DFT value.

III. SUMMARY AND OUTLOOK

The aim of our DFT study has been a discussion of the stability of the tetragonal *Z*-phase VCrN and the cubic—the proposed—compound $VCrN_2$ in competition with binary vanadium and chromium nitrides. Under sufficiently nitrogen-rich conditions $VCrN_2$ appears to be unstable against a phase separation into the binary compounds Cr_2N and V_4N_5, which is a different compound predicted by our study. At nitrogen-poorer conditions, the ternary *Z* phase VCrN is stable. If nonequilibrium conditions prevail in such a way that abundant nitrogen is not bound when the *Z*-phase forms, then a decomposition into binary nitride phases is significantly more probable.

We studied the competition between single-layer stacked (rocksalt variants) and double-layer stacked (*Z* phase) structures, as sketched in Figs. 1 and 4. For the nitrogen-poorest condition corresponding to the composition VCrN, the *Z* phase with pure Cr layer is by far the most stable phase in comparison to the rocksalt variant. For the *Z* phase—according to our DFT approach relaxing all geometry parameters—rather unequal layer spacings are observed [see Fig. 3(b)], which indicate weakening of the bonds between the V-N layers, because their layer distance is increased by about 20% in comparison to a layer stacking with equal distances. The situation is different for nitrogen-richer conditions. Now both structure types are energetically almost degenerate, with the rocksalt variant very slightly more stable by $-0.2\ \mathrm{kJ\ mol^{-1}\ atoms^{-1}}$. Also, the layer distances are much more uniform [see Fig. 3(a)] and, probably, the material is more robust against external loads cutting the bonds between the layers.

All our studies compare energies of isolated bulk phases. The situation in 9%–12% Cr steels is, of course, much more complex because there is the matrix of the steel (essentially Fe) in which the nitrides have to form, and the sizes of the vanadium nitrides are often rather small (in the order of a few nanometers). Furthermore, the binary vanadium nitride commonly forms very fast, whereas the *Z* phase (or another related structurally complex phase) needs a long time before it finally crystallizes. The experimentally observed difficulties in nucleation of *Z* phase compared to VN phases can be reasoned on the basis that nucleation is governed by random compositional fluctuations bringing together Cr, V, and N atoms. In this situation, the probability of forming an fcc nucleus with V and N is many orders of magnitude higher than the probability of finding the atoms in one of the proposed *Z* phase and *Z* phase similar crystal structures. Once a stable VN precipitate has formed, nucleation of a complex *Z*-phase precipitate from this particular compositional fluctuation is made highly unlikely. However, the observed nucleation of *Z* phase on existing VN precipitates is supported by the present simulations since the energetically favorable vacant lattice positions in VN precipitates can be assumed to strongly facilitate the diffusional incorporation of Cr into VN and thus the observed "*in situ*" transformation of VN into *Z* phase.

Comparison with enthalpies of solution obtained from the empirical CALPHAD method shows good agreement with the DFT energies of solution for the *Z* phase and VN. Less good agreement is observed for the Cr_2N, which can be attributed to inaccuracies in the CALPHAD thermodynamic empirical database.

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[1] H. Danielsen and J. Hald, Energy Mater.: Mater. Sci. Eng. Energy Syst. **1**, 49 (2006).

[2] M. Svoboda, J. Bursik, I. Podstranska, A. Kroupa, V. Sklenicka, and K. Mayer, Proceedings of the Conference on Materials for Advanced Power Engineering, 2002, edited by J. Lecomte-Beckers, M. Carton, F. Schubert, and P. J. Ennis (Forschungszentrum, Julich, Germany, Pt. 3, pp. 1521–1530.

[3] W. Binder, ASTM Symposium on Sigma Phase, Cleveland, OH, 1950 (unpublished), Vol. 110, p. 146.

[4] D. H. Jack and K. H. Jack, J. Iron Steel Inst., London **209**, 790 (1972).

[5] A. Strang and V. Vodarek, Mat. Sci. Technol. **12**, 552 (1996).

[6] H. Danielsen, J. Hald, F. Grumsen, and M. Somers, Metall. Mater. Trans. A **37**, 2633 (2006).

[7] H. Danielsen and J. Hald, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **31**, 505 (2007).

[8] N. Saunders and A. Miodownik, *CALPHAD (Calculation of Phase Dia- Grams): A Comprehensive Guide*, Pergamon Materials Series (Pergamon, New York, 1998).

[9] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).

[10] W. Kohn and L. Sham, Phys. Rev. **140**, 1133 (1965).

[11] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[12] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[13] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).

[14] S. Müller, W. Wolf, and R. Podloucky, *Alloy Physics: A Comprehensive Reference* (Wiley, Weinheim, Germany, 2007).

[15] W. Pies and A. Weiss, *Crystal and solid state physics* Vol. 7, Landolt-Börnstein, New Series, Group III (Springer-Verlag, Germany, 1978).

[16] T. Onozuka, J. Appl. Crystallogr. **11**, 132 (1978).

[17] V. P. Zhukov, V. A. Gubanov, O. Jepsen, N. E. Christensen, and O. K. Andersen, J. Phys. Chem. Solids **49**, 841 (1988).

[18] R. Sanjinés, P. Hones, and F. Lévy, Thin Solid Films **332**, 225 (1998).

[19] F. Kubel, W. Lengauer, K. Yvon, K. Knorr, and A. Junod, Phys. Rev. B **38**, 12908 (1988).

[20] P. Lazar, J. Redinger, and R. Podloucky, Phys. Rev. B **76**, 174112 (2007).

[21] H. Ohtani and M. Hillert, CALPHAD: Comput. Coupling Phase Diagrams Thermochem. **15**, 25 (1991).

[22] A. N. Christensen and B. Lebech, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **35**, 2677 (1979).

[23] C. Stampfl and A. J. Freeman, Phys. Rev. B **67**, 064108 (2003).

[24] H. Danielsen and J. Hald, "Z-phase in 9-12% Cr-Steels," Vrmeforsk AB Internal Report No. 863, 2004.

[25] E. Kozeschnik and B . Buchmayr, in *Mathematical Modelling of Weld Phenomena 5*, edited by H. Cerjak and H. K. D. H. Bhadeshia (IOM Communications, London, 2001), Vol. 738, pp. 349–361.

[26] A. D. Mah, US Bureau Mines, Representative Investment Technical Report No. 5529, 1969.