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Structural Vacancies in Compounds of Variable Composition

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The results of studies of compounds of variable composition based on the high-melting metals of the IVa and Va subgroups (oxides, nitrides, carbides, oxide carbides, oxide nitrides, carbide nitrides) have been systematically examined. Problems of atomic ordering in these compounds are discussed, including the development of an inhomogeneous structure and the control of the vacancy concentration while retaining the original chemical composition and type of crystal structure at high pressures and temperatures. The thermodynamics of the formation of structural vacancies in compounds of variable composition are discussed.
The bibliography includes 123 references.

CONTENTS

I. Introduction 1175
II. Atomic ordering in compounds of variable composition 1176
III. Inhomogeneous structure in compounds of variable composition 1176
IV. Filling of structural vacancies in compounds of variable composition 1178
V. Thermodynamics of the formation of structural vacancies 1180

I. INTRODUCTION

Several new compounds of both fixed and variable composition, including compounds with an ordered structure, have been discovered in the last 15–20 years in many well known binary systems of the M–C, M–N, and M–O type (where M is a transition metal from subgroup IVa or Va). Many were obtained by controlling the concentration of vacancies in the crystal lattice, and their distribution. This is true, in particular, of the compounds of the interstitial phase type based on high-melting metals.

The most characteristic feature of compounds of variable composition of this type is the presence of a close-packed sublattice of the pure metal, which acts as a matrix for different atoms accommodated in its interstitial cavities and forming a non-metal sublattice. In this sense the pure metal can be formally treated as a special state of the compound of variable composition in which all the interstitial sites are vacant. In this case the vacant interstitials should be treated as a species equivalent to an interstitial atom rather than as a simple hole in the crystal lattice. When the non-metal sublattice is partially filled the vacant interstitial sites (or structural vacancies) can diffuse through the lattice and behave in some respects like real interstitial atoms.

Structural vacancies, like interstitial atoms, can affect practically all the properties of compounds of variable composition of the interstitial phase type.[1-8] Therefore the defects in the crystal structure should be treated as one of the most important properties of the carbides, nitrides, and oxides of the transition metals, and also of the solid solutions based on them.[1,4-15] These substances, which have a wide homogeneity region, can be described as chemical formations whose composition includes, in addition to metal atoms and non-metal atoms, structural vacancies[5,8] in the non-metal or in the metal sublattice, or in both sublattices simultaneously. It was pointed out[4] in 1969 that vacancies (like metal atoms and non-metal atoms) are independent components of the system and they can affect its properties even more markedly than the atoms.

In addition to "compounds of variable composition", the term "non-stoichiometric compounds" is now generally used in scientific publications, but not always with the same meaning. It has been suggested[4] that the new term is incorrect, since a non-stoichiometric compound has a fixed composition though it is represented by a formula with fractional indices. If we adopt this point of view we must classify the compound $Cu_{31}Sn_8$ (of constant composition) as stoichiometric or as non-stoichiometric according to the method of writing the formula (since simplification produces fractional indices: for example ($Cu_{15.5}Sn_4$ or $Cu_{3.875}Sn$). The same applies to the many organic compounds with a molecular structure, often with a complex chemical composition, which can be expressed by formulae with integral or with fractional indices. Nevertheless their compositions obey the law of multiple proportions, and the compounds are not non-stoichiometric.

In a realistic and soundly based definition[5] of a "non-stoichiometric compound" the concept is associated with the perturbation of the ideal crystal structure. Any compound having a geometrically regular crystal lattice is classified[5] as stoichiometric.

We consider that any compound of fixed composition and having a lattice shown (by diffraction methods) to be ideal should be classified as stoichiometric. The integral indices in the chemical formula of a stoichiometric compound can have any value (not necessarily small), determined from chemical analysis and structural studies. The term non-stoichiometric should be applied to compounds having a homogeneity region, whose width can be determined by analytical methods (mainly, compounds with structural vacancies in their unit cell). The distribution of atoms of different kinds (or of atoms and structural vacancies) in each of the sublattices of a non-stoichiometric compound can be random or ordered.

Clearly, the terms "compound of variable composition" and "non-stoichiometric compound" used in scientific publications have equivalent meanings. The carbides, nitrides, and oxides of the transition metals have wide homogeneity regions and are most correctly referred to as non-stoichiometric compounds of variable composition of the interstitial phase type. This description most fully reflects the special features of the crystalline structure of these substances (the position of the added atoms in the interstitial sites of the metal sublattice, and the presence of a homogeneity region), but the term is too long, and in this review we shall use the shorter term "compounds of variable composition".

II. ATOMIC ORDERING IN COMPOUNDS OF VARIABLE COMPOSITION

It was initially assumed that structural vacancies in the crystal lattice of compounds of variable composition in their homogeneity region are randomly distributed. This belief applied, in particular, to the monocarbides and the mononitrides of the transition metals of subgroups IVa and Va over the whole of their temperature region of existence, as shown in the standard monographs.[1,9,11,12,16] However, ample evidence was subsequently found of the existence of both short-range and long-range order in the crystal lattice of these compounds and of their solid solutions.

Using mainly crystallographic arguments Parthe and Yoon[17] defined eight possible types of ordered structures in carbides: M_2C, M_3C_3, M_8C_5, M_3C_2, M_4C_3, M_5C_4, M_6C_5, and M_8C_7 (where M = Ti, Zr, Hf, V, Nb, Ta). Most of these have already been prepared. In multi-component compounds and in solid solutions the number of possible variants of the structure is, of course, even greater. In the systems M–C, M–N, M–C–O, M–N–O, and M–C–N more than 70 ordered phases have already been discovered: they are formed from the basic structures with face-centred cubic (FCC), body-centred cubic (BCC), and close-packed hexagonal (CPH) crystal lattices. The many superstructures listed in Table 1 were identified by using high-sensitivity diffraction methods (especially neutron diffraction) and lengthy heat treatments (hundreds of hours) at relatively low temperatures (1300 K or less).

The kinetics of the order–disorder transition are largely determined by the previous history of the sample. Thus, the ordering of non-stoichiometric compounds was found[69] to be assisted by the addition of hydrogen. A similar effect was observed[70] after the simultaneous introduction of small amounts of oxygen and nitrogen into the crystal lattice of the hexagonal carbides Nb_2C and V_2C. Reports that ordering is assisted by additions of oxygen, nitrogen, and hydrogen appear also in Refs.71 and 72. In the non-stoichiometric compounds of the V–C system the order–disorder transition was found[73] to depend also on the micro-structure of the sample. Furthermore, two different cubic forms of titanium monoxide $TiO_{1.00}$ have been reported[27] (one of the NaCl type, with a random distribution of vacancies, and another with a partially ordered distribution of vacancies and a 3 times greater lattice constant), stable at 1500–2100 K and 1250–1500 K respectively. A third, monoclinic modification of $TiO_{1.00}$ with a fully ordered distribution of vacancies is stable at temperatures below 1250 K. However, other workers prepared compounds of the TiO_y type at 1270 K [74] and 1070 K,[75] but failed to observe the ordering reported[26,27] for the compound $TiO_{1.00}$ (and also for other TiO_y compositions). Only one cubic structure (NaCl type) was found in the entire homogeneity region by using "preparations in X-ray diffraction equilibrium".

The data in Table 1 suggest that ordering in the non-stoichiometric monocarbides of the group V transition metals produces mainly phases of composition M_6C_5 having monoclinic and trigonal structures. A structural feature common to all ordered phases of the non-stoichiometric monocarbides of the group IV and V transition metals is an alternation of completely filled and partially filled carbon planes in the $[111]_{NaCl}$ or equivalent directions.

In the ordered lower carbides M_2C the characteristic feature is an alternation (in the direction perpendicular to the *c* axis) of carbon planes filled to different extents with carbon atoms.

We also note from Table 1 that the ordered phases of non-stoichiometric cubic titanium, vanadium, and niobium mononitrides have tetragonal structures and differ substantially from the corresponding ordered carbides. In the unit cell of the ordered titanium and niobium nitrides the vacancies are accommodated in the sites of a body-centred tetragonal lattice. In the cubic monoxides different ordered phases can be formed according to the oxygen content and the heat treatment conditions: they have cubic, tetragonal, rhombic, or monoclinic lattices.

The overall conclusion from the data in Table 1 is that ordering phenomena are relatively common in non-stoichiometric compounds of the interstitial phase type, and they are associated with a redistribution of the non-metal atoms over the octahedral interstitials of the metal sublattice.

III. INHOMOGENEOUS STRUCTURE IN COMPOUNDS OF VARIABLE COMPOSITION

The previous history of the sample, which affects the rate of the order–disorder transition, includes the impurities initially present in the materials or introduced during the synthesis, the type and duration of the heat treatment adopted (homogenising, recrystallising, stress relieving), and the chosen cooling regime.

These effects are clearly illustrated by a full and detailed study of short-range and long-range order in the non-stoichiometric niobium carbide NbC_y by NMR,[57,76,78] structural neutron diffraction, X-ray diffraction,[57,58] and magnetic susceptibility.[57,77] It was found that even NbC_y samples quenched from 1800–2300 K contain some short-range order, but the degree of ordering is small. This increases as the temperature is lowered to the transition point, but no long-range order is observed. The structural phase transition, associated with ordering of the carbon atoms and of the structural vacancies in the non-metal sublattice of NbC_y, begins near 1300 K. The NMR spectra for the ^{93}Nb nuclei in NbC_y and the magnetic susceptibility of the niobium carbide samples containing the ordered Nb_6C_5 phase are markedly different from those for the disordered state of niobium carbide.[76–78]

On the other hand the NMR spectra and the magnetic susceptibility are almost unaffected by the amount of ordered phase in the sample, i.e. they are insensitive to the long-range order parameter. It follows[57,77] that in niobium carbide samples containing an ordered phase and prepared with different heat treatment regimes the short-range order parameter α for NbC_y of any composition is almost the same and close to the maximum possible value. This conclusion is confirmed by calculations of α from magnetic susceptibility data.[57,77] Hence the equilibrium state of niobium carbide in the two-phase region near the transition temperature has a high proportion of short-range order, approximately the same in the two phases. On further decrease in the temperature the proportion of disordered phase decreases and finally disappears.

An analysis of the ratio of short-range to long-range order in NbC_y showed[57] that the presence of the maximum possible amount of short-range order for the given composition is a necessary but not a sufficient condition for the appearance of long-range order. It follows that short-range and long-range order can be formed by different mechanisms in niobium carbide: only the long-range interactions (probably, the phonon subsystem) can account for the formation of long-range order, whereas short-range order may be caused

by interactions with a radius of action comparable with the interatomic distance (electronic subsystem).

NMR studies of non-stoichiometric vanadium compounds[79] also detected an effect of the interstitial C, N, and O atoms on the degree of short-range order and on the distribution of vacancies. In VC_y and VN_y the type of short-range order is determined by the mutual repulsion of the vacancies. The insertion of oxygen atoms into the crystal lattice of vanadium monocarbide produces a random distribution of vacancies in a mutually ordered arrangement of carbon and oxygen atoms in the resulting oxide carbide $VC_{0.5}O_{0.5}$. The insertion of hydrogen atoms into VC_y and VN_y does not affect the type of short-range order. Thus we may conclude from that work[79] that the interactions between vanadium atoms and their nearest neighbours are responsible for the formation of short-range order.

The above results (especially those of Ref. 57) show that compounds of variable composition prepared under different conditions can be structurally inhomogeneous. In other words, depending on the synthesis and heat treatment conditions the samples may contain regions in which the ordering differs in extent and in type, and the individual regions may

Table 1. Characteristics of the ordered phases formed in non-stoichiometric carbides, nitrides, and oxides and in their solid solution.

Ordered phase	Type of lattice of the disordered basic phase	Non-metal content, at.%	T_{stab}, K	System	Lattice constants, A	Space group	Refs.
Ti_6O	CPH	~14.5	1090—1100	H	—	—	[18—22]
Ti_3O	CPH	~25.0	~1670	H	$a=5.1411$; $c=9.5334$		[23, 24]
Ti_2O	CPH	~33.3	~1270	H	$a=2.9593$; $c=4.8454$	$P\bar{3}m1$	[23, 24]
$TiO_{0.7}$	FCC	~41.2	870—1260	R	$a=a_0\sqrt{2}$; $b=3a_0/\sqrt{2}$	—	[25, 26]
TiO	FCC	~50.0	~1250	M	$a=9.355$; $b=5.868$; $c=4.135$; $\gamma=107°32'$	$A2/m$	[27]
TiO	FCC	~50.0	1250—1500	C	$a=12.54$	$Fm\bar{3}m$, $F\bar{4}3m$	[27]
$TiO_{1.20}$	FCC	~54.5	~1090	R	$a=2.981$; $b=9.086$; $c=3.986$	—	[27]
$TiO_{1.25}$	FCC	~55.6	~1050	T	$a=6.642$; $c=4.156$	—	[27]
Zr_6O	CPH	~14.3	~1070	H	—	—	[28]
ZrO_y	CPH	~23.0	~710	H	—	—	[29]
Zr_3O	CPH	~25.0	870—1070	H	$a=5.5629$; $c=31.1850$	$R\bar{3}2$	[28]
ZrO_x	CPH	25.9—29.2	~770	H	$a=a_0\sqrt{3}$; $c=c_0$	$R\bar{3}_12$	[30]
Hf_6O	CPH	~14.3	~1070	H	—	—	[31]
$HfO_{1/6}$	CPH	~14.0	~690	H	—	—	[29]
Hf_3O	CPH	~25.0	~1070	H	—	—	[31]
V_6O	BCC	~12.5	—	TC	$a=b=3.114$; $c=2.994$; $\alpha=\beta=90.3°$; $\gamma=90°$	—	[32]
β-V_4O	BCC	16.0—20.0	≤2210	T	$a=2.98$; $c=3.36$	$I4/mmm$	[33]
β'-$V_{16}O_3$	BCC	14.0—16.0	≤940	T	$a=11.96$; $c=6.62$	$I4/mmm$	[33]
ε-V_3O	BCC	22.0—28.0	≤1640	M	$a=16.68$; $b=16.50$; $c=17.60$; $\beta=90°20'$	$P2_1/c$	[33]
γ-V_2O	BCC	32.0—36.0	≤1730	M	$a=32.47$; $b=20.49$; $c=20.56$; $\beta=129°40'$	$C2/m$, $C2$	[33]
$V_{52}O_{64}$	FCC	54.5—56.5	~870	T	$a=11.72$; $c=8.245$	—	[35]
$VO_{1.27}$	FCC	~56.0	<1070	T	$a=16.623$; $c=16.515$	—	[34]
Nb_6O	BCC	~14.3	570—770	T	$a=3.384$; $c=3.274$	—	[36]
Nb_4O	BCC	~20.0	770—970	T	$a=6.65$; $c=3.32$	—	[37]
Nb_2O	BCC	~33.3	670—770	T	$a=6.645$; $c=4.805$	—	[36]
NbO_2	H	~66.6	~1520	T	$a=13.71$; $c=5.985$	$I4_1/a$	[38]
Ta_6O	BCC	~14.3	<770	T	$a=3.363$; $c=3.254$	—	[39, 40]
Ta_4O	BCC	~20.0	<770	R	$a=3.61$; $b=3.27$; $c=3,20$	—	[39]
Ta_2O	BCC	~33.3	>720	T	$a=6.675$; $c=4.721$	—	[39]
δ'-Ti_2N	T	~33.3	~770	T	$a=4.226$; $c=8.452$	—	[41]
δ''-Ti_2N	T	~37.0	≤1070	T	$a=4.144$; $c=8.781$	—	[42]
α-V(N)	BCC	~3.8	~570	R	$a=12.52$; $b=12.10$; $c=2.988$	—	[43]
β-V(N)	BCC	~7.2	~1520	T	$a=a_0\sqrt{2}$; $c=c_0$	—	[39]
α'-V_8N	BCC	~11.0	—	T	$a=b=3.114$; $c=2.994$; $\alpha=\beta=90.5°$; $\gamma=90°$	—	[32]
α''-V_8N	BCC	~11.0	—	T	$a=6.228\sqrt{2}$; $c=2.994$	—	[32]
δ'-VN_y	FCC	44.0—47.0	≤790	T	$a=8.150$; $c=8.150$	—	[44]
δ'-NbN_y	FCC	~43.0	≤1670	T	$a=4.382$; $c=8.632$	$I4/mmm$	[44]
Ta_8N	BCC	~11.1	580—650	T	$a=b=4a_0$; $c=4.024a_0$	—	[45]
$Ta_{38}N_5$	BCC	~11.6	580—650	T	$a=b=6a_0$; $c=2.08a_0$	—	[45]
δ-Ti_2C	FCC	33.0—40.0	≤1470	C	$a=8.634$	$Fd\bar{3}m$	[46]
Ti_8C_5	FCC	37.0—43.0	≤1370	TG	$a=6.115$; $c=14.90$	$R\bar{3}m$	[44]
δ'-TiC_y	FCC	34.2—41.5	670—1460	C	$a=2a_0$	$Fd\bar{3}m$	[47]
δ'-ZrC_y	FCC	39.0—43.0	≤1370	TG	$a=6.630$; $c=16.26$	—	[44]
ZrC_y	FCC	38.6—42.5	670—1470	C	$a=2a_0$	—	[47—49]
β'-V_2C	CPH	~33.0	~1800	H	$a=4.997$; $c=4.658$	—	[50]
V_6C_5	FCC	~45.5	~1370	M	$a=5.09$; $b=10.81$; $c=8.81$; $\gamma=109°47'$	—	[51]
V_6C_5	FCC	~45.5	≤1270	TG	$a=5.09$; $c=14.40$	$P\bar{3}_2$	[52]
δ'-VC_y	FCC	~46.6	≤1500	C	$a=8.330$	$P4_332$	[44]
δ''-VC_y	FCC	45.0—47.0	≤1520	M	$a=a_0\sqrt{3/2}$; $b=a_0\sqrt{6}$; $c=3a_0/\sqrt{2}$; $\gamma=109°28'$	—	[50]
Nb_2C	CPH	~33.3	≤1470	R	$a=10.906$; $b=4.969$; $c=3.096$	$Pnma$	[53, 54]
Nb_2C	CPH	~33.3	>1470	H	$a=a_0\sqrt{3}$; $c=c_0$	—	[53]
Nb_4C_3	FCC	~43.0	—	C	$a=4.440$	—	[55]
Nb_6C_5	FCC	42.8—45.5	—	TG	—	—	[56]
Nb_6C_5	FCC	44.7—46.8	≤1370	M	$a=c=5.4605$; $b=9.4579$; $\alpha=\gamma=90°$; $\beta=109.47°$	$C2/m$	[57, 58, 66]
Ta_2C	CPH	~33.3	<1900	H	$a=a_0$; $c=c_0$	$P\bar{3}m1$	[59]
Ta_4C_3	FCC	~43.0	—	C	$a=4.42$	—	[55]
Ti_2CO	FCC	~41.1	—	C	$a=a=2a_0$	$Fd\bar{3}m$	[60]
$TiC_{0.5}O_{0.5}$	FCC	—	—	C	$a=4.280$	—	[61]
TiC_xN_y	FCC	$x+y\leq 0.72$	—	C	$a=2a_0$	$Fd\bar{3}m$	[48, 49, 62—64]
ZrC_xN_y	FCC	$x+y\leq 0.74$	—	C	$a=2a_0$	$Fd\bar{3}m$	[48, 49, 62—64]
$VC_{0.5}O_{0.5}$	FCC	—	—	M	$a=8.28$; $b=4.14$; $c=4.20$; $\beta=90°41'$	—	[65]
VC_xN_y	FCC	46.6	1300	C	$a=2a_0$	$P\bar{3}_112$	[67]
VC_xN_y	FCC	45.5	1500	TG	$a=a_0\sqrt{3/2}$; $c=2a_0/\sqrt{3}$	—	[68]

Symbols: C, cubic; T, tetragonal; H, hexagonal; TG, trigonal; R, rhombic; M, monoclinic; TC, triclinic; CPH, close-packed hexagonal; BCC, body-centred cubic; FCC, face-centred cubic; a_0, b_0, c_0 are the lattice constants of the disordered basic phase; T_{stab} is the stability range of temperature.

be combined in different ways. The relative amount and size of the regions can also differ between samples. So far these effects in interstitial phases have tended to be ignored, in spite of the extensive data available on this problem in the case of metal alloys (see, for example, Ref.80). The type of structural inhomogeneity in the sample can have a marked influence on the physicochemical properties of the substance: these effects are often incorrectly attributed to electronic factors. In this sense establishing a state close to equilibrium becomes especially relevant to the solution of the fundamental problem in physicochemical analysis: the study of the composition–structure–property dependence.

Most of the alloys and solid solutions used in modern technology are in a hetero-phase state which gives them special physical properties: a high mechanical strength, hardness, and heat resistance, a low electrical conductivity, etc. Many structural and physical studies have shown that the properties of interstitial and of substitutional solid solutions are determined by the morphology, substructure, and nature of the conjugated phases. The required types of substructure are generated by using appropriate methods of heat treatment: quenching, annealing, etc.

Neutron diffraction, X-ray diffraction, and electron microscopic work has shown that hetero-phase structures are very diverse and differ in the shape of the inclusions and in their orientation relative to the crystallographic axes of the host crystal, as well as in their mutual disposition. In metal alloys we often find a periodicity (or a modulation) in the distribution of the inclusions: under these conditions the phase which is precipitated by the decomposition of the cubic (uniform) solid solution can have a similar or a lower symmetry. The periodicity of the distribution of inclusions can be so marked as to generate an additional diffraction pattern.

In terms of conventional thermodynamic considerations the shape of a crystal of the new phase can be related to its surface tension; this point of view suggests that the deposited crystals should be in the form of regular polyhedra. However, in studies of hard alloys based on interstitial phases (carbides, nitrides, carbide nitrides) it was found that the crystals of the new phase often consist of platelets or needles, whereas regular grids are formed by the precipitated phases in metallic alloys. On the other hand from the standpoint of classical thermodynamics as applied to phase transitions the free energy of a two-phase system depends on the total volume of each phase, but not on the relative position of the inclusions or on the area of their faces: it follows that the distribution of the inclusions should be random.

The special features of phase transitions in solids cannot be explained without allowing for the elastic stresses created during the transitions. The orientational relationships, the shape, and the mutual arrangement of the mother phase and of the precipitate are inexplicable otherwise. However, this approach has not so far been adequately explored in respect of non-stoichiometric compounds of the interstitial phase type. One of the few studies of the effect of the elastic deformation energy on the formation of solid solutions of carbides and nitrides[81] established a correlation between the elastic deformation energy, the decomposition temperature of the solid solution, and the possibility of developing short-range and long-range order. In particular it was shown that short-range order is observed in solid solutions of compounds of variable composition when the maximum energy of the elastic deformation is approximately 3–5 kJ mole^{-1}. Thus from a knowledge of the elastic deformation energy we can assess the extent of disturbance of the crystal lattice and the likely type of short-range order, and we can identify hidden regions for the decomposition of the solid solution, which strongly affect the physicochemical properties of these solutions.

IV. FILLING OF STRUCTURAL VACANCIES IN COMPOUNDS OF VARIABLE COMPOSITION

Problems associated with the filling of structural vacancies in the crystal lattice of compounds of variable composition at high temperatures and pressures are of direct interest. The possibility was first suggested as a result of a study[82] of the monoxide FeO_y at high temperature and pressure. It was later shown[83] that defect-free FeO_y can be obtained by the simultaneous application of high pressure (7.74 GPa) and temperature (1920 K) to the material (which contained ~14% of vacancies in each sublattice in its initial state). Large increases in the density and in the lattice constant of the sample were observed. The partial or complete filling of the vacancies as a result of thermo-baric treatment has been observed also in other materials:[84–92] for example, in titanium and vanadium monoxides, in the oxide carbides of titanium, vanadium, and niobium, and in the oxide nitrides of titanium and vanadium (Table 2).

From the data listed in Table 2 we conclude that the vacancies can be filled only by the combined application of high temperature and pressure. Vacancies can be filled in either sublattice up to a predetermined threshold value, when all the sites in the sublattice are occupied by atoms of the appropriate kind and all the vacancies have disappeared. We should stress that vacancy filling is possible only under static loading conditions. Dynamic (shock) compression does not result in the disappearance of structural vacancies. The data in Table 2, like other published results,[84–92] suggest a definite sequence (in space and time) of processes stimulated by the thermo-baric treatment: in other words, they suggest a diffusion mechanism for the filling of vacancies.

The thermo-baric treatment produces not only vacancy filling but also a change in the state of charge of the atoms. This is shown by the fact that the X-ray emission spectra of the samples of composition $TiO_{0.88}$ and $TiO_{1.27}$ have a different shape[6,92] after the thermo-baric treatment (Table 2). The decrease in the concentration of structural vacancies and the change in the charge state of the atoms caused by the application of high temperature and pressure should produce marked changes in the properties of compounds of variable composition. It has long been assumed that the states established at high temperatures and pressures can be studied only under those conditions, because the state is not retained when the pressure is lowered to normal values.

We have shown[88] that the state induced by high temperature and pressure can be preserved indefinitely even under normal conditions: in this way the characteristics of a substance subjected to thermo-baric treatment can be investigated by conventional methods.

The changes in properties are clearly seen in the case of the monoxide $VO_{0.91}$.[93,94] After thermo-baric treatment the magnetic susceptibility (which initially obeyed the Curie–Weiss law) becomes temperature-independent; it also changes by a large amount.[94] A study of the effect of thermo-baric treatment on the electronic structure of $VO_{0.91}$ (by comparing calculations by the SCF MO LCAO method in the MWH approximation with X-ray emission spectra) showed that the change in the parameters of the electronic structure (electronic configuration of the atoms, effective charges, bond occupancies in nearest-neighbour atoms) varies monotonically with pressure. An increase in pressure changes the occupancy of the valency orbitals of vanadium towards the value for the neutral atom. This is confirmed by X-ray emission

data, which indicate, in particular, a decrease in the degree of $p-d$ hybridisation of the wave functions of the vanadium atoms.[93]

The use of high pressures and temperatures, especially in the case of compounds with structural vacancies in both sublattices, has helped to solve another important problem: the preparation of the so-called imaginary compounds whose existence had been predicted by Mendeleev.[95] A detailed discussion of this problem will be found in Refs. 88, 92, and 96–100: we shall only state that the imaginary chemical compound concept is one of the chemical methods of predicting not only the region of existence of compounds of variable composition but also the possibility of preparing new compounds.

Table 3. Conditions for the formation of the cubic carbides V_2C, $VC_{1.0}$, and Nb_2C.

T, K	V_2C (Ref. 108)		$VC_{1.0}$ (Ref. 108)		Nb_2C (Ref. 102)	
	ΔG, kcal mole^{-1}	p, GPa	ΔG, kcal mole^{-1}	p, GPa	ΔG, kcal mole^{-1}	p, GPa
700	0.97	43.6	4.5	92.3	—	—
1000	1.77	79.6	10	205.0	5.0	205.0
1300	2.04	92.7	19	389.5	—	—
2000	—	—	—	—	7.0	285.0
3000	—	—	—	—	11.0	450.0

The crystal-chemical conditions for the production of imaginary chemical compounds in interstitial phases have been formulated:[88,92,98–102] they state that thermo-baric treatment can be used to change the concentration of structural vacancies (up to the complete elimination of vacancies) in one or in two sublattices simultaneously with formation of a stoichiometric compound. Hence, it is pointed out[88,92,98–100] that the stability regions of the cubic carbides and nitrides of subgroup IVa–Va metals can be shifted as far as the compositions M_2C, M_2N (lower limit) and $MC_{1.0}$, $MN_{1.0}$ (upper limit), which are not accessible under normal conditions. The most detailed thermodynamic treatment of this phenomenon will be found in Refs. 101 and 103–106. It has been used in calculations of the thermo-baric conditions of formation of stoichiometric, defect-free titanium monoxide,[103] and zirconium[101,104,106] and vanadium carbides.[105,106]

The writers,[102] using Leipunskii's method[107] in the quasi-one-component approximation, have calculated the formation conditions at high p and T (Table 3) of the cubic modification of the lower niobium carbide Nb_2C, which usually crystallises in the hexagonal system. The free energy difference ΔG between the hypothetical cubic carbide Nb_2C and the hexagonal carbide obtained in practice was identified with the quantity $p\Delta V$, where ΔV is the change in volume of the crystal accompanying the transition between the two modifications (ignoring the baric compression and the thermal expansion of the crystal[102]). The same approach was later used[108] to calculate the conditions for the thermo-baric synthesis of the cubic (NaCl type) V_2C and $VC_{1.0}$ carbides. As Table 3 shows, extreme values of p and T are needed to yield these compounds. The estimated pressures needed to give the cubic modifications of the carbides Nb_2C, V_2C, and $VC_{1.0}$ are probably too high because of the neglect[102,108] of baric and thermal effects. According to our calculations[105,106] the thermo-baric synthesis of the defect-free cubic vanadium carbide $VC_{1.0}$ at 700, 1000, and 1300 K requires pressures of 20, 27, and 37 GPa respectively, i.e. much lower than those given in Ref. 108. Nevertheless all theoretical estimates[101–106,108] of the effect of thermo-baric treatment on compounds

Table 2. Chemical composition, lattice constants (a), density (ρ), and number of formula units in the unit cell (n) of the monoxides, oxide carbides, and oxide nitrides of titanium and vanadium before (I) and after treatment at pressure p and temperature T for time τ (II).

Composition	a, Å		ρ, g cm^{-3}		n		Thermo-baric treatment condition			Refs.
	I	II	I	II	I	II	p, GPa	T, K	τ, min	
$TiO_{0.88}$	4.1890	4.2107	4.93	5.50	3.52	4.01	9.0	1470	2	[84]
$TiO_{1.27}$	4.1667	4.1742	4.79	4.90	3.06	3.15	9.0	1510	3	[84]
$TiC_{0.44}O_{0.57}$	4.2910	4.3080	4.84	5.15	3.70	3.98	9.0	1470	1	[85, 86]
$TiC_{0.22}O_{0.44}$	4.2416	4.2471	4.91	5.00	3.92	4.01	7.74	1970	5	[90]
$TiC_{0.42}O_{0.44}$	4.2864	4.2909	4.82	4.90	3.81	3.92	7.74	1870	5	[90]
$TiC_{0.30}O_{0.74}$	4.2571	4.2739	4.84	5.16	3.55	3.83	7.74	1870	5	[90]
$TiC_{0.19}O_{0.81}$	4.2333	4.2566	4.87	5.22	3.52	3.84	7.74	1870	5	[90]
$TiN_{0.37}O_{0.51}$	4.2270	4.2448	5.14	5.32	3.82	4.00	9.0	1670	2	[85, 86]
$TiN_{0.45}O_{0.28}$	4.2260	4.2329	5.07	5.14	3.93	4.00	7.74	1270	5	[89]
$TiN_{0.32}O_{0.40}$	4.2206	4.2260	5.07	5.10	3.91	3.96	9.0	1870	5	[89]
$TiN_{0.22}O_{0.46}$	4.2110	4.2222	5.10	5.15	3.93	4.00	9.0	2070	5	[89]
$VO_{0.91}$	4.0447	4.1203	5.70	6.21	3.48	4.00	9.0	1870	1.5	[88]
$VO_{0.97}$	4.0574	4.1030	5.63	6.10	3.41	3.82	9.0	1870	1.5	[88]
$VO_{1.01}$	4.0689	4.1073	5.62	5.90	3.40	3.67	9.0	1770	1.5	[88]
$VO_{1.07}$	4.0874	4.1123	5.53	5.75	3.34	3.54	7.74	1670	2	[88]
$VC_{0.62}O_{0.16}$	4.1307	4.1519	5.64	5.75	3.78	3.93	7.74	1670	7	[87]
$VN_{0.56}O_{0.21}$	4.0820	4.0920	5.94	6.02	3.92	4.00	9.0	2070	1.5	[91]
$VN_{0.57}O_{0.33}$	4.1100	4.1351	5.89	6.03	3.84	3.99	9.0	2070	1	[91]
$VN_{0.46}O_{0.50}$	4.1161	4.1375	5.77	5.92	3.71	3.87	9.0	2070	1	[91]
$VN_{0.51}O_{0.46}$	4.1203	4.1351	5.89	5.98	3.73	3.87	9.0	1870	2	[91]

of variable composition lead to the same conclusion: the concentration of vacancies can be lowered, and new modifications of the compounds can be produced, by using this treatment.

On the whole, both the experimental and the theoretical studies of compounds of variable composition under thermobaric conditions so far reported indicate the possibility (previously unknown) of controlling the properties of a substance only by changing the concentration of vacancies in the unit cell while retaining the initial composition and structure type.

V. THERMODYNAMICS OF THE FORMATION OF STRUCTURAL VACANCIES

It is clear from the above discussion that structural vacancies should be distinguished from the point defects of the vacancy type usually discussed in the literature, which are formed either at high temperatures (thermal vacancies) or by irradiation (Frenkel defects).

In the description of point defects[109] the energy of formation of the vacancies (E) is assumed to be constant: under these conditions the change in the free energy of the crystal due to the formation of n vacancies is

$$\Delta G = nE - T\Delta S \qquad (1)$$

where ΔS is the entropy change resulting from the addition of n vacancies to the crystal. In the case of point defects the contribution of the vibrational component of the entropy to ΔS is assumed to be negligibly small (on the evidence of experimental data on thermal vacancies). Therefore the quantity ΔS is practically equal to the configurational component of the entropy, i.e.

$$\Delta S = k \ln \frac{N!}{n!\,(N-n)!} \qquad (2)$$

where N is the number of sites in the crystal and k is Boltzmann's constant.

By minimising the free energy and simplifying we can obtain from Eqns.(1) and (2) the following expression for the concentration of point defects of the thermal vacancy type:

$$c = \frac{n}{N} = \exp\left(-\frac{E}{kT}\right) \qquad (3)$$

The energy of formation of thermal vacancies in metal and metal-like compounds is $E \cong 1$ eV (for example, E is 1.27, 1.10, and 0.95 eV in copper, silver, and gold respectively[110]). At room temperature this value of E corresponds to a very low relative number of thermal vacancies ($c \cong 10^{-17}$), i.e. the average distance between thermal vacancies is of the order of a millimetre. At 2000 K the equilibrium relative number of vacancies becomes $c = 2 \times 10^{-3}$. Hence, as reported,[109] the equilibrium concentration of thermal vacancies in metals is negligibly small even near the melting point.

In compounds of the interstitial phase type such as transition metal carbides, nitrides, and oxides a high concentration of structural vacancies is a characteristic property, and the concept of point defects in these materials is almost meaningless.[111] Furthermore, in compounds of the interstitial phase type (for example, oxides) vacancies can exist in two sublattices at the same time (the non-metal and the metal sublattice); vacancies in the two sublattices have different effects on the properties of the compound.[112] Obivously, the vacancies in compounds of variable composition have a non-thermal origin, and their formation is closely related to the structural properties of the interstitial phase: these vacancies are therefore now called structural.

The presence of a large number of structural vacancies in compounds of variable composition has a marked effect on the vibrational entropy, which cannot be neglected in this case. The thermodynamic description of non-stoichiometric compounds allowing for the formation of structural vacancies[2,3,9,13,14,113–116] is based on the following considerations.

Consider a compound (in equilibrium at some temperature T) consisting of i non-equivalent sublattices each containing n_i vacancies and N_i filled sites. The free energy $\Delta G(n)$ of such a crystal at constant pressure can be written[3]

$$\Delta G(n) = \Delta G + \sum \int_0^{n_i} \Delta H_i \, \mathrm{d}n_i - T\left(\Delta S_\kappa + \int_0^{n_i} \Delta S_i \, \mathrm{d}n_i\right) \qquad (4)$$

where $\Delta G = \Delta H - T\Delta S$ is the free energy of the defect-free crystal, ΔH is the heat of formation of the defect-free crystal, ΔS is the change in entropy accompanying the formation of the defect-free crystal, ΔH_i is the energy of formation of the structural vacancies in the i-th sublattice of the crystal, ΔS_i is the change in vibrational entropy due to the formation of vacancies in the i-th sublattice, and

$$\Delta S_\kappa = k \sum \ln[(N_i + n_i)!/N_i! n_i!]$$

is the change in the configurational component of the entropy on formation of the vacancies.

It follows from (4) that the heat of formation of a crystal containing structural vacancies is

$$\Delta H(n) = \Delta H + \sum \int_0^{n_i} \Delta H_i \, \mathrm{d}n_i \qquad (5)$$

and the entropy change is

$$\Delta S(n) = \Delta S + \Delta S_\kappa + \sum \int_0^{n_i} \Delta S_i \, \mathrm{d}n_i \qquad (6)$$

Eqn.(4) can therefore be written in terms of the free energy of formation of the structural vacancies:

$$\Delta G_i = \Delta H_i - T\Delta S_i \qquad (7)$$

In general Eqn.(4) assumes a dependence of ΔH_i and ΔS_i on the concentration of structural vacancies, i.e. it assumes interactions between the vacancies. Assuming that ΔS_i is negligibly small and that no interaction takes place between the vacancies (i.e. adopting the weak defect interaction approximation) gives a change in the energy of formation of vacancies proportional to their number, so that Eqn.(4) reduces to Eqn.(2). Thus formula (2) is a special case of Eqn.(4) which can be used to describe the behaviour of both structural vacancies and point defects; the parameters of this description are the quantities ΔH_i and ΔS_i.

On reaching the equilibrium vacancy concentration for the given temperature $c_i = n_i/N_i$ the free energy $\Delta G(n)$ goes through a minimum, i.e. $\partial \Delta G(n)/\partial n_i = 0$. Using this condition in conjunction with the Stirling formula for the series expansion of ΔS_i we obtain from (4), after simplification, an expression relating the equilibrium concentration of structural vacancies in the i-th sublattice to their energy of formation and to the vibrational component of the entropy:

$$kT \ln c_i = -\Delta H_i + T \cdot \Delta S_i \qquad (8)$$

It follows from (8) that at any temperature above the absolute zero the vacancies are thermodynamically stable and their concentration can be decreased indefinitely but not brought to zero. Furthermore, if ΔH_i and ΔS_i are constant and independent of the number of structural vacancies we can expect a linear relationship between $\ln c_i$ and T^{-1}.

Data on the congruent evaporation of titanium and zirconium nitrides have been used[117,118] to determine the energies of formation of structural vacancies in the nitrogen sublattice

of these compounds on the assumption that vacancy interactions are negligible: the result (expressed for one molecule) was 0.94 ± 0.32 and 1.13 ± 0.06 eV respectively. The change in the vibrational component of the entropy caused by the formation of vacancies in zirconium nitride was found[118] to be (0.31 ± 0.04) × 10^{-3} eV K^{-1}. However, the calculation[118] of the heat of formation ΔH°_{298} and of the free energy of formation ΔG°_{298} of zirconium nitride in its homogeneity region from the observed energies of formation and vibrational entropy changes of the structural vacancies gave a discrepancy between experiment and calculation increasing with the number of nitrogen vacancies and reaching 25% at the lower boundary of the homogeneity region. The discrepancy was attributed[118] to the neglect of the concentration dependence of the energy of formation of the vacancies. A comparison of experimental and calculated values of the activity of carbon in the homogeneity region of zirconium carbide similarly led to the conclusion[119] that satisfactory agreement between experiment and calculation is obtained only by allowing for the dependence of the energy of formation of the vacancies on the composition of the compound.

A detailed analysis[13,14,115] of existing experimental data on the congruent evaporation of a series of carbides and nitrides with a structure of the NaCl type has shown that the dependence of $\ln c$ on T^{-1} is non-linear, and therefore that a change in defect density in these materials affects either the energy of formation of the vacancies, or the vibrational component of the entropy, or both, i.e. that vacancy interactions are present.

In compounds of variable composition with an NaCl type structure each metal atom is octahedrally surrounded by six sites of the non-metal sublattice which form the first coordination sphere; the second coordination sphere consists of twelve metal atoms. Let us consider a compound containing structural vacancies in only one of the sublattices (for example, the non-metal sublattice). We shall assume that the interaction between the non-metal atoms is limited to the first coordination sphere. When all the sites in the non-metal sublattice are filled the energy of formation of the vacancies will be denoted by ΔH_1, and the vibrational component of the entropy by ΔS_1. If all the sites of the non-metal sublattice adjacent to a given non-metal atom are vacant we shall use the symbols ΔH_2 and ΔS_2. In general, when some of the sites are occupied by non-metal atoms but some (n) are vacant, the energy of formation of the vacancies can be expressed as the sum

$$\Delta H_n = (1-n)\Delta H_1 + n\Delta H_2 \qquad (9)$$

Similarly, we can write for the vibrational component of the entropy

$$\Delta S_n = (1-n)\Delta S_1 + n\Delta S_2 \qquad (10)$$

If only the vibrational component of the entropy increases with the defect density, by inserting (10) into (4) and solving the resulting equation we obtain an expression for the equilibrium concentration of vacancies which allows for the dependence of ΔS_B on the number of vacancies in the homogeneity region of the compound:

$$kT \ln c_i = (1-n)T\Delta S_1 + nT\Delta S_2 - \Delta H \qquad (11)$$

If only the energy of formation of the vacancies ΔH_B varies with the number of defects the corresponding expression is

$$kT \ln c_i = T\Delta S - (1-n)\Delta H_1 - n\Delta H_2 \qquad (12)$$

Lastly, if both ΔH and ΔS are dependent on the defect density we have

$$kT \ln c_i = (1-n)T\Delta S_1 + nT\Delta S_2 - (1-n)\Delta H_1 - n\Delta H_2 \qquad (13)$$

Eqns.(11)–(13) assume the existence of a self-consistent solution for the equilibrium concentration of vacancies c_i at a given temperature T for known values of the parameters $\Delta H_{1,2}$ and $\Delta S_{1,2}$.

Thus even allowing for interactions only in the non-metal sublattice and assuming a simple linear dependence implies considering three types of solution and determining which of these solutions best describes the experimental data.

The quantities ΔH_1, ΔH_2, and ΔS_1, ΔS_2, have been determined,[13,14,115] and their statistical significance in describing the equilibrium concentration of structural vacancies in titanium, zirconium, and niobium carbides and nitrides by Eqns.(11)–(13) has been assessed by using the Fisher criterion, F.[120] By comparing the dispersion obtained for each of these equations with the F criterion we obtain a statistical proof of the dependence of the energy of formation of vacancies and of the vibrational component of the entropy on the defect density of the compound; this suggests the presence of interactions between the vacancies, in keeping with earlier data.[57,76,68,79] An analysis of these results[13,14,115] also showed that the allowance for the dependence of the vibrational component of the entropy on the number of structural vacancies is more important than the corresponding correction for the energy of formation of the vacancies. As the defect density increases, the energy of formation of vacancies ΔH_B in the carbides and nitrides of titanium, zirconium, and niobium decreases (Table 4), denoting the presence of mutual repulsion between the vacancies.

Table 4. Energies of formation of structural vacancies ΔH_B and changes in the vibrational component of the entropy ΔS_B in the formation of structural vacancies in non-stoichiometric compounds.

Compound	ΔH_B, eV	$10^3 \Delta S_B$, eV K^{-1}	Refs.
ZrC_{1-n}	0.524—0.520n	0,009—0.318n	[13, 115]
VC_{1-n}	0.150	0,010	[3]
NbC_{1-n}	0.532—0.411n	—0,002—0,089n	[115]
TiN_{1-n}	1.347—0.401n	0,415—0.241n	[14]
ZrN_{1-n}	1.867—0.614n	0,726—0.462n	[13,14]

The quantities ΔH_B and ΔS_B for vanadium carbide were determined[3] in the approximation of non-interacting atoms, because the precision of the experimental data on the heat of formation of vanadium carbide was insufficient to determine the dependence of the energy of formation of the vacancies and of the vibrational entropy on the number of vacancies. The temperature dependence of the free energy of formation of the vacancies in the carbon sublattice for the vanadium carbide VC_y (for one formula unit of the compound) was found to be[3]

$$\Delta G, \text{ eV} = 0.415 + 1.574 \cdot 10^{-3} T + 7.553 \cdot 10^{-8} T^2 - 0.17 \lg T - 0.458 \cdot 10^{-3} T \lg T + 4.522\, T^{-1}$$

In compounds with defects in both sublattices, such as the cubic modifications of titanium and vanadium monoxides, for which congruent evaporation data are not available, the energy of formation of the structural vacancies can be calculated by using Eqn.(5). An attempt to calculate the energy of formation of vacancies in titanium monoxide has been reported.[121] However, no attempt was made to evaluate

the precision of the experimental data on the heat of formation of TiO_y in the homogeneity region, and as a result the form of the dependence of the energy of formation of the vacancies on the defect density of the metal and of the oxygen sublattice was incorrectly chosen; the results[121] cannot therefore be treated as reliable. In Refs.2 and 116 the energies of formation of the metal and the oxygen vacancies in TiO_y and VO_y are calculated by using the methods of mathematical statistics to allow for the precision of the experimental data, giving more meaningful results.

It follows from Eqn.(5) that the heat of formation of the crystal containing defects ($\Delta H(n)$) can be expressed in terms of the heat of formation of the defect-free crystal (ΔH) and the energy of formation of vacancies in each of the sublattices. For the monoxides of vanadium and titanium (compounds with a double set of defects) we have

$$\Delta H(n) = \Delta H + \int \Delta H_M \, d n_M + \int \Delta H_O \, d n_O \qquad (14)$$

where ΔH_M and ΔH_O are the energies of formation of vacancies in the metal and the oxygen sublattice respectively.

The form of the dependence of ΔH_M and ΔH_O on the composition of the compound is not known, but these quantities can be determined by using existing experimental data on the composition dependence of the heats of formation in the homogeneity regions of titanium and vanadium monoxides[111,122] in conjunction with structural data[23,123] for these compounds. In the zeroth approximation we assume that the energy of formation of the vacancies is independent of the composition of the compound: this gives

$$\Delta H(n) = \Delta H + \Delta H_M n_M + \Delta H_O n_O \qquad (15)$$

According to (15) the heats of formation of the monoxides should be directly proportional to the numbers of defects in the metal and in the oxygen sublattice. However, it has been shown experimentally that the dependences deviate from linearity and have a point of inflection near the equiatomic composition.[111,112] The deviations may be due to experimental error, or to the dependence of the interatomic bond energy on the composition of the monoxides, resulting in a change in the energy of formation of the vacancies in the homogeneity region of the compound.

To allow for possible interatomic interactions we shall assume that ΔH_M depends on the interaction between metal atoms and ΔH_O on the interaction between oxygen atoms in the first coordination spheres of the metal and oxygen atoms respectively. Let ΔH_{M_1} and ΔH_{O_1} be the energies of formation of vacancies in the metal and in the oxygen sublattice in the perfect (defect-free) lattice of the monoxide, and let ΔH_{M_2} and ΔH_{O_2} be the energies of formation of vacancies in the metal and the oxygen sublattice when all the sites in the metal or the oxygen sublattice adjacent to the given metal or oxygen atom are vacant. In general, when only some of the lattice sites are occupied by metal or oxygen atoms, the energy of formation of metal and oxygen vacancies can be expressed as (as was done for the carbides and the nitrides) as a sum of the products of ΔH_{M_1} and ΔH_{M_2} (or ΔH_{O_1} and ΔH_{O_2}) by the fractional number of filled and of empty sites in the metal (or in the oxygen) sublattice:

$$\Delta H_M = (1-n_M)\Delta H_{M_1} + n_M \Delta H_{M_2};$$
$$\Delta H_O = (1-n_O)\Delta H_{O_1} + n_O \Delta H_{O_2}$$

Allowing for the nature of the dependence of ΔH_M and ΔH_O on the concentration of vacancies, four variants of the description of the heat of formation of a crystal containing defects in terms of the energy of formation of the vacancies in each of the sublattices are possible. According to (14) these variants correspond to the following cases: 1) the energies of formation of vacancies ΔH_M and ΔH_O are constant and independent of the vacancy concentration; 2) only ΔH_M varies with the concentration of vacancies, whereas ΔH_O stays constant; 3) ΔH_O varies, and ΔH_M stays constant; 4) ΔH_M and ΔH_O vary simultaneously. The Fisher criterion F has been used[2,116] to identify which of these four assumptions has the highest probability, i.e. gives the best description of existing experimental data allowing for their precision. By comparing the dispersion with the value of the F criterion it was shown that in the case of titanium monoxide the energies of formation of the vacancies in both sublattices are dependent on the concentration of the appropriate defects. Clearly, a similar dependence can be expected in vanadium monoxide, but the precision of the experimental data[112] on the heat of formation of VO_y in the homogeneity region is too low to establish this fact unambiguously. The energies of formation of structural vacancies in the metal and the oxygen sublattice of titanium monoxide TiO_y are ΔH_M, eV $= -15.104 - 1.225\, n_M$ and ΔH_O, eV $= -2.068 + 12.678\, n_O$ respectively.[116] For the vanadium monoxide VO_y the energy of formation of vacancies in the metal and in the oxygen sublattice is $\Delta H_M = 5.32$ eV and $\Delta H_O = 8.172$ eV respectively.[2]

Thus by treating structural vacancies as analogues of interstitial atoms we can describe non-stoichiometric compounds in terms of a simple thermodynamic model. The change in the energy of formation of vacancies in the homogeneity regions of these compounds allows us to identify the nature of the interatomic interactions. Knowing the energy of formation of structural vacancies in the carbides, nitrides, and oxides of the transition metals we can calculate the synthesis conditions of the defect-free compounds.[101,104-106]

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The above discussion shows that structural vacancies in compounds of variable composition can be treated as analogues of interstitial atoms: for example, the deviation from stoichiometry can be wholly described as the formation in the nonmetal sublattice of a substitutional solution whose components are interstitial atoms and structural vacancies. Evidently, the defect state of the crystalline structure, i.e. the presence of a high concentration of structural vacancies, is the most important property of compounds of variable composition of the interstitial phase type.

The presence of a large number of structural vacancies offers some additional flexibility in the controlled synthesis of compounds of variable composition having prescribed properties. One possibility is to use a thermo-baric treatment to vary the vacancy concentration while preserving the initial composition and structure of the compound. Another means of fine control of all the properties of a compound of variable composition relies on the redistribution of the interstitial atoms and vacancies over the sites of the nonmetal sublattice. The study of vacancy distributions is of direct scientific interest because it offers a key to an understanding of the nature of interatomic interactions in compounds of variable composition. This is because the rearrangement of atoms and vacancies in a crystal lattice is a manifestation of interactions at the atomic level. So far the effect of the nature of the vacancy distribution on the properties of non-stoichiometric compounds has not been adequately studied, but we consider this approach to be very promising from a practical as well as a scientific aspect.

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