Translated from *Uspekhi Khimii*, 48, 2262 - 2280 (1979) U.D.C. 541.12.034.2 + 536.5

Transformations in Refractory Compounds, Brought about by High Pressures and Temperatures

Yu.G.Zainulin, S.I.Alyamovskii, and G.P.Shveikin

The influence of high pressures and temperatures on the structural characteristics of the refractory carbides, nitrides, and monoxides of the transition metals have been examined. The results have been discussed in the light of one of the components of Kurnakov's theory of daltonides and berthollides—the concept of imaginary compounds, developed by Bokii. A number of new ideas following from this examination have been formulated. It has been shown that at high pressures and temperatures it is possible to obtain new electronic modifications of compounds and to extend considerably the range of existence of phases of variable composition. It has been shown that the concept of imaginary compounds is correct, and it has been suggested that a large number of imaginary compounds are realised at high pressures and temperatures. Other methods of obtaining imaginary compounds have been recommended. The bibliography contains 109 references.

CONTENTS

I.	Introduction	1225
II.	Carbides	1225
III.	Nitrides	1228
IV.	Monoxides	1228
V.	Oxide carbides and oxide nitrides	1230
VI.	Summary	1230

I. INTRODUCTION

In recent years there has been considerable interest in the study of processes taking place in a solid under the simultaneous influence of high pressures (p) and temperatures (t). This is due because it is thus possible to bring about various transformations (polymorphic transformations, decomposition and reduction of a substance, perfection and ordering of a crystal structure, transitions from the crystalline state to the amorphous and vitreous states, production of the metallic state, changes in the electronic structure of compounds and the valency state of atoms, the synthesis of periodic and "imaginary" compounds, the production of new electronic modifications of known compounds, etc.); see for example Refs. 1–34.

In the present work an attempt is made to examine systematically the influence of high p and t chiefly on refractory carbides and nitrides and partly on oxides of the transition metals and their reciprocal solid solutions.

The compounds discussed, which are formed chiefly from metals of sub-groups IVa–Va, belong to the class of so-called interstitial phases and are distinguished by a number of characteristic features, which it is appropriate to discuss briefly. Firstly, most of these compounds (which exhibit the properties of metals or covalent crystals) have wide homogeneity ranges, and their unit cells sometimes contain a large number of structural vacancies in one part (for example the monocarbides of the transition metals of groups IV and V, and Fe monoxide) or both parts (for example the cubic NaCl-type monoxides of Ti and V, and the oxide carbides and oxide nitrides of Ti, Zr, Hf, V, and Nb). The metal atoms of these compounds often exhibit cubic or hexagonal close packing, with the non-metal atoms arranged in the octahedral sites. Under certain conditions, some interstitial phase compositions exhibit ordering ($NbC_{0.75}$, $TaC_{0.75}$, $TiO_{1.00}$, $TiC_{0.5}O_{0.5}$, $VC_{0.5}O_{0.5}$, etc.). More detailed data on interstitial phases are given in a number of monographs (see for example Refs. 35–38).

II. CARBIDES

The first report of the influence of high pressures† on carbides, including those of refractory metals, is found in papers dealing with the synthesis of artificial diamonds. In these papers (reviewed, for example, in Refs. 2, 23, and 40), carbides are used as the carbon-containing material, which liberates carbon at high p and t as a result of chemical reactions.

The first special study of the influence of high pressures on the refractory carbide (and nitride) of titanium TiC (and TiN), of unknown composition, was carried out by Bridgman[40], who determined the compressibility and electrical resistance at a pressure $p = 1.2 \times 10^4$ kg cm^{-2} and found that the electrical resistance decreased with increase in pressure; no structural transformations were recorded. Semerchan and coworkers[41] studied the influence of pressure (up to 10^5 kg cm^{-2}) and temperature (1400°) on the hard alloy T15K6 (composition, wt.%: Ti 12.5, C 7.5, Co 6.0, Fe 0.1, remainder W). The specimens in the form of cylinders of diameter 6 mm and height 8 mm were kept under these conditions for 5 min in the apparatus previously developed[42]. The heating was then stopped, and when the temperature had decreased to ambient the pressure was also removed. The alloy treated in this way consisted of three phases—the carbide WC, a solid solution of tungsten carbide in titanium carbide TiC–WC, and a solid solution of tungsten (up to 3%), titanium (up to 0.5%), and carbon (up to 0.5%) in cobalt, Co(W, Ti, C). (Semerchan and coworkers[41] report that the loss of carbon by the specimens during this treatment was prevented, but they do not describe how this was achieved.) The experimental data are given in Table 1.[41] The decrease in the specific gravity of the treated specimens compared with the original specimens

† In accordance with the published classification[39], high pressures correspond to $p \geq 10^4$ kg cm^{-2}.

was attributed[41] to the filling of the cracks by katlinite—the medium in direct contact with the specimen, used to transmit the pressure. The decrease in the lattice spacing of the phase TiC–WC is related to the additional solution (up to 5 wt.%) of WC in TiC. In the X-ray diffraction patterns of the treated alloy, the diffraction maxima were broader, and their point character, observed for the original specimen, had disappeared. All this was attributed[41] to the production of distortions in the crystal structure of the carbide phases.

Table 1. Influence of high pressure and temperature on the characteristics of the alloy T15K6.[41]

Characteristics of the specimens	Original alloy	Treated alloy
Specific gravity, g cm^{-3}	11.25	11.0–11.48
Average particle size of the phase WC, μm	3.46	3.65
Average particle size of the phase TiC–WC, μm	3.60	3.56
Concentration of graphite inclusions in the field of view, %	up to 0.5	up to 0.5
Porosity, %	up to 0.2	up to 0.2
Vickers hardness, kg cm^{-2}	1480	1480–1100
Lattice period of the phase TiC–WC, A	4.3119	4.3105
Width of the 420 diffraction line of the phase TiC, min	63	92
Width of the 202 diffraction line of the phase WC, min	80	153

Pivovarov and coworkers[43] subjected specimens of the hexagonal carbide $WC_{0.99}$ to all-round compression (up to ~100 kbar) with simultaneous heating (up to 2130°C). Under these conditions, the diffraction maxima became appreciably broader (the width of the 211 line increased from 6 mradian to 26 mradian). Moreover, this treatment led to a significant increase in the micro-hardness (from 1800 kg mm^{-2} to 2800–3200 kg mm^{-2}). These results were attributed to an increase in the density of dislocations and other defects in the crystal lattice, leading to plastic deformation of the carbide $WC_{0.99}$.[43] When the specimen was annealed to 1800° for 1.5 h, the micro-hardness decreased to 1870 kg mm^{-2}; at the same time, the width of the diffraction line decreased to 14 mradian. The same effects were observed by Koval'skii and coworkers[44], when the carbides WC, TaC, TiC, NbC, ZrC, and Cr_3C_2 were treated for 3 min under conditions of quasi-hydrostatic pressure (p = 100 kbar) with simultaneous heating to 1400°; part of the carbides contained up to 3 wt.% cobalt. These data[44] are given in Table 2. Koval'skii and coworkers[44] also drew attention to the marked increase in the micro-hardness and the broadening of the X-ray lines after treatment. In this case, in contrast to the earlier data[43], annealing did not lead to a significant change in the micro-hardness of pure tungsten carbide (the conditions of annealing, however, were slightly different from those described in Ref. 43, see Table 2). The addition of cobalt leads to a marked increase in the rate at which the hardness decreases, as a consequence of the participation of the liquid phase in the recrystallisation (see Table 2), including that in WC.

Unlike Koval'skii and coworkers[44], Samsonov and coworkers[45] were able to achieve a significant increase in the micro-hardness of specimens of titanium carbide TiC treated under conditions of quasi-hydrostatic pressure in the range 25–80 kbar and temperatures in the range 1000–2000°. The specimens were first heated in cells to the required temperature, kept at this temperature for 3 min, and then compressed for 1 min. The maximum micro-hardness achieved in the compressed titanium carbide[45] was 3300 kg mm^{-2}.

Table 2. Characteristics of the alloys studied by Koval'skii and coworkers[44].

Parameters	Original specimens								
	TiC+Co	ZrC	NbC+Co	NbC	TiC+Co	WC+Co	VC	Cr_3C_2+Co	Cr_3C_2
Micro-hardness, kg mm^{-2}:									
original specimen	2400	2900	1800	1800	1600	1800	1800	1350	1350
treated specimen	2500	2900	2600	2600	2200	3100	3100	2600	2600
after annealing*	2400	3000	1800	2100	1700	1900	3000	1700	2200
Broadening of the lines, radian	8.75×10^{-4}	1.75×10^{-3}	1.31×10^{-2}	1.16×10^{-2}	1.05×10^{-2}	1.13×10^{-2}	2.33×10^{-3}	9.35×10^{-3}	8.20×10^{-3}

* Annealed at 1400° for 3 h.

Samsonov and coworkers[46] applied static and dynamic pressures to specimens of hexagonal tungsten carbide WC_x (x = 0.85, 0.90, 0.95) and mixtures of the metal and carbon black with the same compositions. Shock compression was applied in retaining ampoules; the pressure at the front of the leading wave was $(1.45–1.65)\times10^6$ kg cm^{-2}. The quasi-hydrostatic pressure treatment was carried out at 1200° and 90 kbar for 30 min. X-Ray phase analysis and measurement of the micro-hardness of the specimens treated in this way revealed individual granules and conglomerates of granules of the cubic modification of WC.[46] The formation of the cubic carbide WC was observed on compression of both the original carbides ($WC_{0.90}$ and $WC_{0.95}$) and the mixtures of tungsten and carbon black having the same compositions. Explosive shocks[46] also led to decomposition of the original hexagonal carbide $WC_{0.95}$ to metallic tungsten, hexagonal W_2C and cubic WC. An interesting feature is that it has been reported[47] that high-temperature cubic WC, synthesised under ordinary conditions, has a restricted range of existence with respect to both composition ($WC_{0.61-0.67}$) and temperature (2530–2747°).

Sevast'yanova and coworkers[48] synthesised cubic tungsten carbide under conditions slightly different from those used by Samsonov and coworkers[46]. Hexagonal tungsten carbide and a mixture of finely divided metallic tungsten and carbon black in equi-atomic proportions were subjected to high pressures (35–70 kbar) and temperatures (1400–2000°). The duration of treatment was varied from 1 min to 3 min. In addition, the original specimens contained 0.1–2 at.% of stabilisers—metals of groups IV and V and their cubic carbides TiC, ZrC, and VC. When hexagonal tungsten carbide was used as starting material, the cubic carbide could not be obtained, even when stabilisers were added. It was formed, however, by compressing a mixture of the metal and carbon black containing TiC. The lattice period of the cubic phase, determined from the 220 line for one of the heterophase specimens, was 4.336 Å. This large value of the lattice period was attributed to the formation of a solid solution WC–TiC.

Clougherty and coworkers[49] treated an equi-atomic mixture of metallic molybdenum and carbon, and also Mo_2C and carbon, at high temperatures (1800–2500°) and pressures (40–70 kbar). X-Ray phase analysis of the resulting specimens showed the presence of ten additional lines, in addition to those of the phases existing under ordinary conditions. All were indexed in a cubic face-centred lattice with period $a = 4.27$ Å. This carbide was assigned the stoichiometric composition MoC, with four metal atoms in the unit cell[49]. Cubic molybdenum carbide synthesised under ordinary conditions exists in a different composition range ($MoC_{0.66-0.76}$) at temperatures of 1960–2600°.[50,51]

Table 3. Characteristics of MoC_x specimens[52].

Compn. of original specimen	Phase compn. of original specimen	Phase compn. after treatment* (lattice periods of individual components)
$MoC_{0.567}$	$Mo_2C + \eta$-MoC_x (hexagonal)	$Mo_2C + \eta$-MoC_x ($a = 3.02$ Å; $c = 14.41$ Å)
$MoC_{0.661}$	$Mo_2C + C$	η-$MoC_x + Mo_2C$
$MoC_{0.661}$	$Mo + C$	η-$MoC_x + Mo_2C$
$MoC_{0.733}$	α-MoC_x (cubic)	η-MoC_x ($a = 3.011$ Å; $c = 14.63$ Å)
	η-MoC_x (hexagonal)	α-MoC_x

* Treatment at 25 kbar and 1500° for 14 min.

Table 4. Characteristics of specimens obtained by Dubrovskaya and Nazarova[53].

Original specimens				Treated specimens ($p = 120$ kbar, $t = 1500°$, $\tau = 30$ min)			
compn. of mixture	concentration of carbon, wt.%		a, Å	concentration of carbon, wt.%		a, Å	concn. of nitrogen, wt.%
	combined	free		combined	free		
$Nb_{0.95}Mo_{0.05}C$	11.0	0.28	4.4646	—	нет	4.4674	0.1
$Nb_{0.85}Mo_{0.15}C$	10.73	0.60	4.4528	10.38	0.17	4.4420	—
$Nb_{0.71}Mo_{0.29}C$	10.62	0.95	4.430	9.59	0.02 0.63	4.4341 4.4344	—
$Nb_{0.51}Mo_{0.49}C$	9.63	1.57	4.3926	9.68 8.88	1.02 1.22	4.3926 4.3897	—
$Nb_{0.30}Mo_{0.70}C$	8.90	1.64	4.3417	—	0.88	4.3629	—
$Nb_{0.15}Mo_{0.85}C$	7.94	2.42	4.295	—	1.01	4.319 4.3273	—

The behaviour of the carbide phases in the Mo–C system at high pressures was also studied by Shinyaev and coworkers[52]; heterophase alloys of molybdenum and carbon, and their mixtures having the composition $MoC_{0.661}$, were treated for 40 min at 25 kbar and 1500° in an apparatus of the "anvil with indentation" type (see Table 3). X-Ray diffraction study after treatment showed that all the specimens contained the hexagonal η-carbide. Its lattice periods in the specimen having the composition $MoC_{0.567}$ differed considerably from those of the carbide synthesised under ordinary conditions ($a = 3.006–3.011$ Å; $c = 14.61–14.64$ Å).[50,51] It was concluded[52] that the homogeneity range of η-MoC_x is extended towards lower concentrations of carbon at high p and t. In addition, a thermodynamic calculation[52] showed that a pressure of 25 kbar lowers the decomposition temperature of the hexagonal η-carbide from 1650° to 1380°.

Dubrovskaya and Nazarova[53] tried to achieve additional introduction of carbon into the lattice of the solid solutions $NbC_{1.0}$–$MoC_{0.67}$ to obtain specimens having compositions close to the stoichiometric. Mixtures of the solid solutions and free carbon were treated at a pressure of 120 kbar and 1500° for 30 min. Chemical analysis of these specimens showed a decrease in the concentrations of both free and combined carbon. An interesting feature is that the lattice period, compared with the original value, remained unchanged for one of the specimens, decreased for another, and increased for the remainder (see Table 4).

The all-round compression of a substance can also be brought about under dynamic conditions. Compression by explosion leads to various transformation in a solid[10,11,13,15,17,20,24,27,54]. The influence of pressure pulses on refractory compounds has been studied by a number of workers[55–60,62]. Appreciable micro-porosity has been reported[55] in various specimens subjected to compression by explosion, including TiC, ZrC, NbC, and WC. The X-ray diffraction patterns (particularly those of the ZrC, NbC and WC specimens show diffuse broadening of the lines, indicating that the crystal structure is imperfect. In addition to the lines due to the original phases the X-ray diffraction patterns of the carbides ZrC, NbC, and WC, recorded after compression by explosion[55], contained extra reflections (in the case of WC these lines belong to hexagonal α-W_2C), the intensity of which increased with increased strength of the shock wave. It was concluded[55] that partial decomposition of the carbides NbC, ZrC, and WC takes place. The X-ray density of the compressed specimens remained unchanged[55].

The increase in the strength of the hard alloy WC–Co (15 wt.% Co) under the influence of an explosion (pressure 105–230 kbar) has been studied[56]. The micro-hardness of the original alloy (1200–1365 kg mm^{-2}) and the carbide (1824–1994 kg mm^{-2}) increased sharply after compression: to 2173–2311 kg mm^{-2} for the alloy, and to 2954–3200 kg mm^{-2} for tungsten carbide. These results show satisfactory agreement with results obtained by other workers[44]. The density of the alloy increased[56] from 13.6 g cm^{-3} to 14.5 g cm^{-3}, and the tungsten carbide particle size decreased. A phase transformation in metallic cobalt from the hexagonal to the cubic modification was also observed[56].

The influence of dynamic compression (67–190 kbar) on the structure of the carbides of titanium (TiC_x; $x = 0.62$, 0.75, 0.83, 0.98), zirconium (ZrC_x; $x = 0.62$, 0.72, 0.80, 0.96), and niobium (NbC_x; $x = 0.72$, 0.82, 0.90, 0.99) in their ranges of existence has been studied[57]. The compression was carried out in cylindrical and annular retention ampoules. Hexagen, pentaerythritol tetranitrate, and fused trinitrotoluene were used as explosives. The X-ray diffraction patterns of the carbides, recorded after shock compression, showed broadening of the diffraction maxima[57]. In addition, some of the specimens showed an increase in micro-hardness (by 6.8% for $TiC_{0.62}$, 20% for $NbC_{0.72}$, 14.3% for $NbC_{0.82}$, 11.1% for $NbC_{0.9}$, and 11.6% for $NbC_{0.90}$) after the effect of the explosion. This indicated[57] the passage of plastic deformation in local volumes, which was also related to the increased density of dislocations in the compressed specimens.

The influence of shock waves (160–350 kbar) on the physicochemical characteristics of technical zirconium carbide (Zr 87.75%, $C_{combined}$ 10.15%, C_{free} 0.1%, Fe 0.35%, Mg 0.01%) has been studied[58]. The dimensions of the regions of coherent scattering, the degree of distortion of the crystal lattice, the pyknometric density, and other characteristics of both the original and the compressed specimens were determined. The pyknometric density remained unchanged (6.45 g cm^{-3}) up to a pressure of 160 kbar, then increased to a maximum (6.51 g cm^{-3}) at 160 kbar, and finally decreased up to a pressure in the shock front equal to 350 kabr, reaching a minimum value (6.37 g cm^{-3}). The lattice period of the phase remained unchanged at $a = 4.688 \pm 0.002$ Å. The increase in the pyknometric density was attributed[58] to a decrease in the concentration of defects as a result of the "collapse" of micro-cracks and micro-cavities.

The influence of pressure pulses on the carbides of chromium (850 kbar) and molybdenum (1.05 Mbar) has been studied[59]. In one of the original heterophase specimens containing Cr_7C_3 and Cr_3C_2, the explosion led to rupture of the ampoule. X-Ray phase analysis of the products showed the presence of the higher carbide $Cr_{23}C_6$ in addition to the original phases. The carbide Mo_2C, however, decomposed to Mo and α-MoC_x on compression. These results were attributed to a change in the electronic structure of the original phases under the influence of high pressures.

III. NITRIDES

There is very little published information on the influence of all-round compression on refractory nitrides. The effect of shock waves on the nitrides of niobium, zirconium, silicon, chromium, and gallium has been studied[60]. Cylindrical steel retention ampoules were used, and the explosive was hexagen. The nitrides of Zr and Si did not show structural transformations[60], but the crystal structure of chromium nitride became less perfect; gallium nitride decomposed. Under the influence of the shock wave, the original hexagonal nitride $NbN_{0.98\pm0.03}$ was converted into the cubic nitride δ-$NbN_{0.83\pm0.10}$ with lattice period 4.39 ± 0.01 Å and density 7.20 ± 0.01 g cm^{-3} (density of the original niobium nitride 7.932 ± 0.006 g cm^{-3}). This change in density was attributed to latent micro-porosity in the $NbN_{0.83}$ subjected to shock compression[60].

Cubic (NaCl type) tantalum nitride with lattice period $a = 4.358 \pm 0.001$ Å has been synthesised[61] at $p = 30$–100 kbar and $t = 1800°$. This nitride is fairly stable: the polymorphic transformation to a phase having the WC structure, stable under ordinary experimental conditions, took place only after heating for 4 h in a vacuum (10^{-5} mmHg) at 1200°. It was assumed[61] that the composition of the nitride obtained differs from the stoichiometric composition, since the temperature of its conversion into the superconducting state ($T_c = 6.5$ K) is lower than that for tantalum carbide, whereas in the isomorphous niobium carbide and nitride the opposite T_c ratio is observed: 17.3K for NbN and 11.0 K for NbC.[61]

Samsonov and coworkers[62] applied dynamic pressure (~ 3 Mbar) to powdered hexagonal stoichiometric tantalum nitride ($TaN_{1.0}$) and detected a cubic (NaCl type) phase with $a = 4.33$ Å in addition to the hexagonal phase. Samsonov and coworkers assigned to it the composition $Ta_{0.8}N(TaN_{1.25})$ and reported the presence of vacant sites in the metallic sublattice ($\rho_{expt} = 15.652$ g cm^{-3}) although this does not follow from the original data (calculation gives the values of 3.85 and 4.81 for the numbers of tantalum and nitrogen atoms respectively).

The action of high pressures (up to 80 kbar) and temperatures (up to 2000°) does not lead to structural changes in the nitride VN or in mixtures of the nitrides TaN and Ta_2N.[63]

IV. MONOXIDES

Before examining published data on the influence of high p and t on the monoxides TiO_x and VO_x, titanium oxide carbides and oxide nitrides, and iron monoxide, it should be noted that all these phases exhibit appreciable homogeneity ranges and have structural vacancies in both sublattices (only FeO_x has vacancies confined to the metal sublattice); see for example Refs. 35–38.

Table 5. Change in the lattice periods, density, and percentage of vacancies in $TiO_{1.0}$ with change in pressure and temperature[67].

Pressure	Temperature (°C) and conditions of preparation	Lattice period at 25°C, A	Density, measured at 25°C, g cm^{-3}	Concn. of vacancies, %	No. of atoms in the cell	
					n_{Ti}	n_O
1 bar	1725 (original specimen)	4.1784	4.97	14.0	3.42	3.42
1 bar	1500 (2 d)	4.1796	4.97	14.4	3.42	3.42
1 bar	1500 (2 d) + 1200 (3 d)	4.1812	—	—	—	—
1 bar	1100	4.1817	—	—	—	—
9.4 kbar	1100	4.183	—	—	—	—
30.2 kbar	1100	4.1907	—	—	—	—
36.3 kbar	110	4.1922	5.01	12.9	3.47	3.47
1 bar	1320	4.1805	—	—	—	—
15 kbar	1320	4.1862	5.03	13.0	3.48	3.48
39.3 kbar	1320	4.1938	—	—	—	—
56.4 kbar	1320	4.2013	—	—	—	—
77.4 kbar	1550	4.2064	5.68	0.0	3.99	3.99
1 bar	1650	4.1788	—	—	—	—
20.9 kbar	1650	4.1877	5.01	13.2	3.47	3.47
27.4 kbar	1650	4.1916	5.04	12.4	3.50	3.50
35.0 kbar	1650	4.1945	—	—	—	—
56.4 kbar	1650	4.2025	—	—	—	—
56.4 kbar	1650	4.2020	—	—	—	—
61.6 kbar	1650	4.2045	—	—	—	—
66.2 kbar	1650	4.2038	5.37	5.88	3.76	3.76
77.4 kbar	1650	4.2062	5.69	0.0	3.99	3.99

The decomposition of iron(II) oxide under the influence of hydrostatic pressure (10^4 kg cm^{-2}) has been studied[64]. The original FeO specimen with $a = 4.294$ Å was subjected to pressure and isothermal heating at 400, 450, 480, 500, 550, and 590°C. The products of the decomposition of wüstite ($aFeO \xrightarrow{p,t} bFe + cFe_3O_4 + dFeO$), obtained under pressure, contain much larger quantities of the metallic phase than specimens prepared without using high pressure (other conditions being the same).[64] The explanation given for this difference[64] is that in the first case the iron ions may partly fill the vacancies in the metal sublattice of FeO (since pressure generally decreases the rate of diffusion processes), forming chiefly the metallic phase. This was proved[64] by X-ray diffraction, magnetic measurements, metallography, and chemical analysis. The synthesis of stoichiometric wüstite $FeO_{1.00}$ by the reaction between $Fe_{0.95}O$ and Fe at high pressures (> 36 kbar) and temperature (770°) has been reported[65].

The simultaneous influence of high pressure (up to 78.1 kbar) and temperature (from 880° to 1650°) on the monoxide $TiO_{1.00}$ (a_{init} = 4.1784 Å and 4.1796 Å) has been studied[66,67]. At a pressure of 77.4 kbar and temperatures of 1550° and 1650°, the unit cell of this phase became complete (that is contained no structural vacancies). The gradual decrease in the concentration of vacancies with change in p and t [67] is shown in Table 5. The number of atoms in the unit cell was determined[67] from data on the composition and lattice periods, and from the density of the specimens, measured by flotation, hydrostatic weighing, and powder pyknometry. Table 5 shows that increase in pressure leads to a regular increase in the lattice period and density, and to a decrease in the number of vacancies.

With increase in pressure to ~60 kbar at room temperature[68], the lattice periods of specimens of non-stoichiometric $Ti_{0.82}$ and $TiO_{1.25}$ decrease. The same results were obtained for wüstite[69]. The authors cited[69], however, were not convinced that the vacancies were filled under the conditions of their experiment. In fact, calculations[69] showed that the disappearance of the vacancies, as observed in Ref. 67, should lead to an increase in a after treatment of the specimens, whereas the values of a for the monoxide specimens, including FeO, acquired practically their original value after the high pressure was removed.

The equilibrium concentration of structural vacancies in TiO at high pressures and temperatures has been calculated[70] by the methods of statistical thermodynamics. The calculations indicate that the concentration of vacancies decreases from 14.5% at a pressure of 1 bar to ~10–14% at 100 kbar.

Subsequent experiments[71,72] confirmed the chief results of the previous studies on the filling of the vacancies in titanium monoxide, and also gave new data. Specimens of TiO_x in the homogeneity range (x = 0.86–1.24) were subjected to all-round compression at p = 50–60 kbar and t = 1100–1300°.[71] This led to a considerable decrease in the number of vacancies in both sublattices of TiO_x (see Table 6). The same result was obtained[72] by treating specimens of $TiO_{0.88}$ and $TiO_{1.27}$ at p = 90 kbar and t = 500–1300°. The lattice periods of these specimens increased sharply compared with the original specimens (Table 7), and this was attributed to filling of the structural vacancies in the metal sublattice ($TiO_{0.88}$) and oxygen sublattice ($TiO_{1.27}$) to give complete lattices.

An interesting result was obtained by Zainulin and coworkers[72] who found that a specimen of $TiO_{1.27}$, synthesised at $t > 1300°$, consisted of three phases, unlike other specimens. Its X-ray diffraction pattern, in addition to the lines of the cubic monoxide with a = 4.230 Å, showed a phase with interplanar spacings close to those for orthorhombic TiO_2(II),[73] and tetragonal TiO_2. The latter was readily indexed in a structure of the rutile type with lattice periods a = 4.575 Å, c = 3.080 Å, c/a = 0.673. These values differ considerably from the values corresponding to rutile stable under ordinary conditions: a = 4.59373 Å, c = 2.95812 Å, c/a = 0.64395.[75] In the opinion of the authors cited[72], this indicates that at p = 90 kbar and $t > 1300°$, the $TiO_{1.27}$ specimen decomposes to TiO_2 and a Ti_2O phase having a lower oxygen content than $TiO_{0.88}$. In fact, according to Ehrlich[74], the lattice period (and the intensity ratio I_{111}/I_{200}) of the monoxide TiO_x obtained under ordinary conditions increases with decrease in the oxygen concentration over its homogeneity range. According to the data obtained by Zainulin and coworkers[72], $a(TiO_{0.88})$ (for p = 90 kbar and t = 1020° and 1200°) is smaller than the period of the cubic lattice in the two-phase specimen of $TiO_{1.27}$; the same applies to the ratio I_{111}/I_{200}.

Table 6. Influence of pressure and temperature on the structural characteristics of the phase TiO_x.[71]

x in TiO_x	Characteristics of the original TiO_x: density, g cm^{-3}	lattice period, A	number of atoms in cell: n_{Ti}	n_O	Conditions of experiment: p, kbar	t, °C	Characteristics of the compressed TiO_x: density, g cm^{-3}	lattice period, A	number of atoms in cell: n_{Ti}	n_O
0.86	5.057	4.189	3.63	3.12	60	1300	5.117	4.205	3.72	3.20
0.89	5.043	4.191	3.60	3.20	50	1100	5.162	4.200	3.71	3.30
0.90	5.029	4.190	3.58	3.22	60	1300	5.129	4.207	3.70	3.33
0.91	5.025	4.186	3.56	3.24	60	1300	5.083	4.203	3.64	3.31
0.95	5.054	4.185	3.52	3.34	50	1300	5.177	4.200	3.66	3.48
1.00	5.000	4.184	3.45	3.45	50	1300	5.058	4.200	3.54	3.54
1.01	4.984	4.181	3.43	3.47	60	1300	5.043	4 196	3.50	3.54
1.03	4.929	4.173	3.35	3.45	60	1300	5.064	4.200	3.51	3.62
1.06	4.975	4.174	3.36	3.56	60	1100	4.996	4.196	3.43	3.64
1.07	4.975	4.174	3.36	3.60	60	1300	5.032	4.193	3.44	3.68
1.10	4.947	4.178	3.32	3.65	60	1300	5.013	4.192	3.40	3.74
1.12	4.947	4.176	3.30	3.70	60	1300	5.000	4.190	3.37	3.78
1.13	4.921	4.173	3.27	3.70	60	1300	4.969	4.189	3.34	3.78
1.17	4.914	4.174	3.24	3.79	60	1300	4.963	4.188	3.30	3.86
1.18	4.907	4.173	3.22	3.80	60	1300	4.934	4.187	3.26	3.85
1.22	4.851	4.171	3.14	3.83	60	1300	4.942	4.182	3.23	3.94
1.24	4.870	4.170	3.14	3.90	50	1300	4.938	4.198	3.25	4.03

Table 7. Characteristics of the original specimens and the specimens obtained at a pressure of 90 kbar and different temperatures[72].

Compn. and characteristics of the original phase	t, °C	Duration of treatment, min	Phase compn. of compressed specimen	Type of lattice	Lattice period, A	No. of formula units (n) in cell
$TiO_{0.88}$; a=4.1890 Å; n=3.52	500	2	single-phase*	FCC*	4.189	—
ditto	1020	1	single-phase	FCC	4.2107	3.98
»	1200	2	single-phase	FCC	4.2170	4.01
$TiO_{1.27}$; a=4.1667 Å; n=3.06	720	3	single-phase	FCC	4.1742	3.15
ditto	1240	1	single-phase	FCC	4.1740	3.14
»	1300	2	three-phase	1) FCC	4.23	—
				2) tetragonal (rutile type)	a=4.575; c=3.080	—
				3) orthorhombic (α-PbO_2 type)	a=4.531; b=5.498; c=4.900	—

* The lines at large angles on the X-ray diffraction pattern are indistinct.
** Face-centred cubic.

Indirect evidence of the decomposition of the $TiO_{1.27}$ specimen was also obtained by Banus and coworkers[71], who obtained a very large cubic lattice period for a single-phase specimen of $TiO_{1.27}$ (see Table 6); this diverged considerably from the general $a = f(x)$ relationship. This value of a can probably be attributed to the decomposition of $TiO_{1.24}$ to TiO_x ($x \ll 1.24$) and TiO_2; because of the small quantities present, however, the presence of TiO_2 could not be detected by X-ray diffraction.

The influence of dynamic pressure on titanium monoxide has also been studied[76,77]. The following mixtures were subjected to shock compression[76] (p ~ 800 kbar,

$t \sim 1730°C$): $Ti + TiO_2 = 2TiO_{1.0}$; $2Ti + 3TiO2 = 5TiO_{1.2}$ $3Ti + 2TiO_2 = 5TiO_{0.8}$. The reaction products in all cases contained a cubic (NaCl type) phase with lattice periods equal to 4.177–4.179 Å, 4.169 Å, and 4.188 Å respectively. The subsequent action of shock waves on the monoxide synthesised in this way did not alter the lattice periods[76]. Similarly, no significant change in the concentration of structural vacancies was observed when $TiO_{0.84}$, $TiO_{1.06}$, and $TiO_{1.28}$ were subjected to shock compression at pressures up to 600 kbar.[77]

Table 8. Change in the structural characteristics of the vanadium monoxide phase under the influence of pressure $p = 60$ kbar and $t = 1300°C$.[78]

x in VO_x	Characteristics of the original VO_x				Characteristics of the original VO_x			
	density, g cm^{-3}	lattice period, A	number of atoms in cell		density, g cm^{-3}	lattice period, A	number of atoms in cell	
			n_V	n_O			n_V	n_O
0.86	5.736	4.034	3.506	3.015	5.816	4.043	3.589	3.087
0.88	5.752	4.039	3.515	3.093	5.797	4.054	3.579	3.150
0.94	5.677	4.053	3.451	3.244	5.732	4.066	3.518	3.307
0.96	5.674	4.058	3.445	3.307	5.751	4.068	3.518	3.377
0.99	5.602	4.068	3.401	3.367	5.650	5.084	3.471	3.436
1.02	5.583	4.077	3.388	3.456	5.658	4.086	3.456	3.525
1.09	5.507	4.099	3.340	3.641	5.581	4.104	3.349	3.650
1.15	5.419	4.120	3.292	3.786	5.458	4.124	3.326	3.825
1.20	5.371	4.130	3.249	3.899	5.402	4.133	3.275	3.930
1.23	5.329	4.133	3.209	3.947	5.374	4.133	3.236	3.980

Specimens of vanadium monoxide ($a_{init} = 4.0738$ Å) have been subjected to the simultaneous influence of high pressures (56.4 kbar) and temperatures (1650°).[67] An increase in the lattice period (due to the filling of vacancies) to 4.1004 Å and even 4.1295 Å was observed[67]. A similar result was obtained by other workers[78] who subjected specimens of cubic vanadium monoxide VO_x ($x = 0.86–1.23$) to a pressure of 60 kbar and $T = 1300°$ under static conditions. The results of these experiments[78] are given in Table 8; the lattice period increases considerably, and the degree of defect character of the phase decreases. An interesting feature is that, in spite of the high pressure and temperature of treatment ($p = 56.4$ kbar, $t = 1650°$), the lattice period of the monoxide NbO (which can be regarded as crystallising in a NaCl structure with 25% ordered vacancies) remains unchanged[67].

Stable zirconium and tantalum monoxides cannot be synthesised under ordinary conditions (vacuum or inert medium, high temperatures).[79] Zainulin and coworkers[80] attempted to prepare ZrO and TaO. The experiments were carried out at $p = 77$ kbar and $t = 800–1250°$ for 10 min under static conditions in a standard compartment[81]. Specimens of the corresponding oxides were first heated at a reduced pressure of 1.3×10^{-7} mmHg and $t = 1400°$ for 10 h, after which the resuling powders were placed in cylinders of Ta (for the TaO specimen) or zirconium (for the ZrO specimen). The products of the reaction of the mixture of Ta and Ta_2O_5 contained an unknown phase, which crystallised in the orthorhombic system ($a = 11.35$ Å, $b = 8.199$ Å, $c = 8.396$ Å). The mixture of Zr and ZrO_2 treated at 950° contained small quantities of a cubic phase isostructural with NbO. Comparison of the volumes (V) of the starting materials and final products of the reaction $Zr + ZrO = 2ZrO$ ($-\Delta V/V = 4.9\%$) and $3Ta + Ta_2O_5 = 5TaO$ ($-\Delta V/V = 12.2\%$) showed that these reactions should take place with a decrease in V. It was therefore suggested[80] that it is possible in principle to obtain the monoxides TaO and ZrO at high p and t.

V. OXIDE CARBIDES AND OXIDE NITRIDES

Specimens of the cubic oxide carbide $TiC_{0.44}O_{0.57}$ and oxide nitride $TiN_{0.37}O_{0.51}$ have been subjected to all-round compression under quasi-hydrostatic conditions at $p = 90$ kbar and $t = 620–1400°$ (Table 9).[82] The lattice periods of the specimens of the oxide carbide and oxide nitride treated at $p = 90$ kbar and $t = 1200–1400°$ are significantly greater than the original values (Table 9). This result, together with the results of the pyknometric determination of the densities, led to the conclusion[82] that the structural vacancies in the unit cell of these phases are filled. An interesting feature is that in the oxide carbide $TiC_{0.44}O_{0.57}$, both sublattices are complete, whereas in the oxide nitride only the metal sublattice is completely filled. There are no other published data on the influence of high p and t on the characteristics of phases of this kind.

Table 9. Change in the structural characteristics of titanium oxdie carbide and oxide nitride under the influence of pressure $p = 90$ kbar and different temperatures[82].

Composition and characteristics of original phase	t, °C	Duration of treatment, min	Phase compn. of compressed specimen	Type of lattice	Lattice period, A	No. of formula units (n) in the cell
$TiC_{0.44}O_{0.57}$; a=4.2910 A; n=3.70	620	3	single-phase	FCC*	4.2912	3.70
ditto	1200	1	single-phase	FCC	4.308	3.98
$TiN_{0.37}O_{0.51}$; a=4.2270 A; n=3.82	700	2	two phases of the same type	FCC	4.21 4.23	—
ditto	1200	4			4.239	3.99
»	1400	2	single-phase single-phase	FCC FCC	4.2448	4.00

* Face-centred cubic

VI. SUMMARY

Before discussing the above results, it is appropriate to mention briefly one of the component parts of Kurnakov's theory of daltonides and berthollides—the concept of "imaginary" compounds[83]. Kurnakov, in an examination of the chemical character of berthollides, postulated the following possible treatments:

a) berthollides are definite compounds in a state of dissociation;

b) berthollides are solid solutions of definite compounds, unstable in the free state;

c) berthollides are solutions of polymorphic modifications of the components, unstable in the free state.

The term definite compounds is here understood to mean chemical compounds of constant composition, which obey the law of simple and multiple proportions. In accordance with this, Kurnakov proposed three types of equilibrium diagram (Fig. 1). The compounds AB_n, AB_{n_1}, AB_{n_2} which are unstable in the free state and which obey

the laws of stoichiometry, and the modification of the component B_1, were later, at Ageev's suggestion[83,85], called "imaginary". Kurnakov, referring to the method of finding imaginary compounds and modifications, warned that considerable difficulties are encountered in attempts to distinguish these cases experimentally; this can be done only tentatively, by comparing with analogous systems in which the singular ordinate AB_n (Fig. 1*b*) or the second modification (B_1) of the component B (Fig. 1*c*) can be observed directly. In other words, it is necessary to assume the existence, in a given system A–B, of an imaginary compound AB_n, AB_{n_1}, AN_{n_2} or an imaginary modification B_1 if these phases are present in an analogous system.

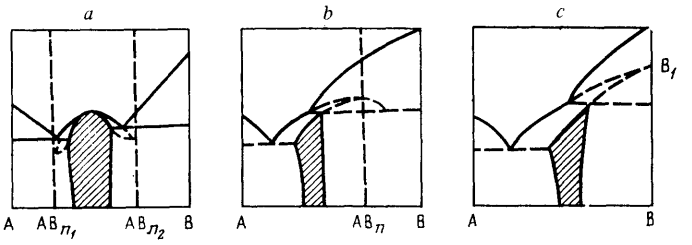


Figure 1. Types of equilibrium diagram with imaginary compounds and an imaginary modification of a component according to Kurnakov, formed: *a*) by isomorphous mixing of non-existent compounds or definite compounds unstable in the free state, AB_{n_1} and AB_{n_2}; b) from a compound AB_n which is unstable or non-existent in pure form; *c*) from a second (B_1) modification of component B, unstable in the free state.

Subsequently, these ideas of Kurnakov were developed in detail by many workers (see for example Refs. 83–97). The nature of imaginary compounds not realised under ordinary conditions was first developed from the structural viewpoint by Bokii[91]. Bokii regarded berthollides as phases of variable composition, in which the limiting degree of filling of the regular system of points (RSP) of the structure is not achieved. In other words, if the processes of substitution, introduction, and removal of atoms under given experimental conditions do not reach the limits characteristic of a given structure, the limiting rational composition is not realised in these phases. In Bokii's opinion, this composition, corresponding to the imaginary compound, can readily be determined by extrapolating the curve characterising the change in the RSP to the composition at which the RSP is completely filled (although this composition will lie beyond the limits of the homogeneity range). It should be noted that in Kurnakov's work[83], for berthollides with and without a maximum on the "composition–property" diagram, two (Fig. 1*a*) and one (Fig. 1*b*) limits respectively were noted, corresponding to the imaginary compound. According to Bokii[91], however, any curve (on the "composition–property" diagram) which does not end at a component or at a compound can be continued in both directions as far as the corresponding compound. In Kurnakov's opinion, the determination of the composition of imaginary compounds on the "composition–property" curve requires the availability of the maximum number of points (in order to carry out the extrapolation over the shortest possible distance), whereas according to Bokii[91], the composition of the imaginary compound can readily be determined from only one point, and the position on the curve, characterising the change in the RSP, at which this extremal point is situated is not important. It is only in the case of a berthollide with a maximum that it is necessary to use two points, since the change takes place in two RSP.

From the foregoing, and with allowance for the ideas put forward by Zainulin and coworkers[82], it is possible to explain various results obtained using high pressures and temperatures, in particular data[49,52,53,65–67,71–73,82] which indicate broadening of the homogeneity range of various phases. Thus stoichiometric cubic (NaCl type) molybdenum carbide, synthesised at high p and t and unstable under ordinary conditions, is the limiting compound at which the RSP is completely filled. In this connection, from data obtained[49] at high p and t, the upper limit of the range of existence of the phase MoC_x must be assigned the composition $MoC_{1.0}$ (under ordinary conditions, the carbide $MoC_{0.76}$ is obtained[50,51]).

A composition close to the limiting composition is observed[98,99] for cubic rhenium carbide ReC (a = 4.005 Å), synthesised at p = 160–180 kbar and t = 1000° (τ = 2–5 min), which cannot be obtained under ordinary conditions. For various monocarbides of metals of sub-groups IVa–VIa, the compositions with the maximum saturation by carbon correspond to the formula $MC_{<1.00}$. The composition $MC_{1.00}$ for these compounds can also be realised at high p and t. It may be noted that the specific values of p and t required to achieve the limiting composition with respect to non-metals cannot always be chosen immediately. Thus in the opinion of Boiko and Popova[61], the composition of cubic tantalum nitride, obtained for the first time, is not stoichiometric; this is also indicated by other data[62].

This in the case of carbides and nitrides with the NaCl structure, the maximum concentration of the non-metal is characteristic of the compositions $MC_{1.0}$ and $MN_{1.0}$ (or, with allowance for complete filling of the RSP, M_4C_4 and M_4N_4). The question of the lower boundary of the homogeneity range of these phases is of interest. From structural considerations[91], for the NaCl structure it should correspond to the compositions $M_2X(M_4X_2)$ or, less probably, M_4X. (The carbide Nb_4C has been obtained[100], but its formation is apparently due to impurities). It should be noted that the carbide $TiC_{0.5}$ [101] and the nitrides $TiN_{0.42}$ [102] and $ZrN_{0.5}$ [103] can be obtained even under ordinary experimental conditions. However, there are as yet no data on carbides and nitrides of analogous composition for other transition metals, synthesised at high p and t. As noted by Bokii[91], the width of the homogeneity range of a phase naturally is not always determined by purely structural factors; it is also influenced by the valency state of the atoms.

Mention must also be made of the oxides of various refractory metals. As already noted, at high temperatures and pressures, increase in these parameters leads to an increase in both the lattice period of the phases TiO_x and VO_x and their densities (for a given composition), due to the filling of the vacancies in the unit cell of the monoxides. Here, however, there is also a change in the charge state of the atoms. In fact for example, the complete monoxide $TiO_{1.00}$, in

contrast to the defect structure apparently contains no M–M bonds, since the M atoms are completely shielded by oxygen atoms[104]. The X-ray emission spectra of compressed specimens of $TiO_{0.88}$ (90 kbar, 1200°, 3 min) and $TiO_{1.27}$ (90 kbar, 1240°, 1 min) also indicate a change in the charges on the atoms[105].

In Batsanov's opinion[54], a change in the charge is also responsible for the increase in the lattice periods of NdF_3 after shock compression (a_{init} = 7.035 Å, c_{init} = 7.211 Å, a_{compr} = 7.066 Å, c_{compr} = 7.230 Å). Batsanov also gave the same explanation for the observed increase[105] in the lattice periods of Co and Ni subjected to dynamic compression.

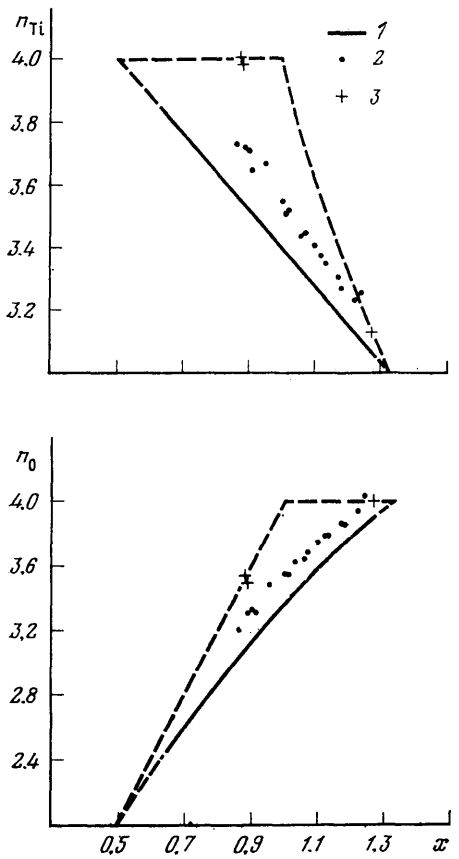


Figure 2. Limits of the change in the degree of filling of the unit cell of the phase TiO_x (range of existence of electronic modifications of titanium monoxide); *1*) data from Ref. 79 for the phase TiO_x synthesised under ordinary conditions; *2*) and *3*) data from Refs. 67 and 72 for the phase TiO_x obtained at high *p* and *t*.

In the homogeneity range of titanium monoxide[82,97], it is possible to distinguish three imaginary compounds: $Ti_2O(Ti_4O_2)$, Ti_3O_4, and $TiO_{1.0}(Ti_4O_4)$ with filled metal, non-metal, and both sublattices respectively. The compounds Ti_3O_4 and Ti_4O_4 can be regarded as already realised[67,71]. As far as the compound $Ti_2O(Ti_4O_2)$ is concerned, it has been noted[82] that it may correspond to the cubic phase detected in the decomposition of $TiO_{1.27}$ (90 kbar, 1300°, 2 min). The same imaginary compounds are revealed in the homogeneity range of VO_x. Up to the present, however, it has been possible to synthesise only the monoxide having an almost completely filled non-metal sublattice, with the composition $VO_{1.23}$ [78] (instead of $VO_{1.33}$).

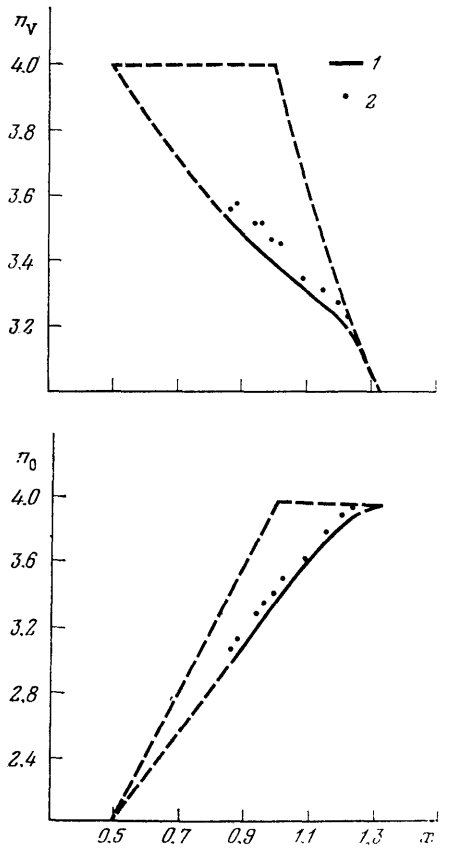


Figure 3. Limits of the change in the degree of filling of the unit cell of the phase VO_x (range of existence of electronic modifications of vanadium monoxide); *1*) data from Ref. 79 for the phase VO_x synthesised under ordinary conditions; *2*) data from Ref. 78 for the phase VO_x obtained at high *p* and *t*.

Thus in the case of phases having dual defect character, it is possible, by filling the structural vacancies in one or both sublattices (by the action of high temperatures and pressures), without changing the composition, to obtain compounds with different concentrations of electrons in the unit cell, that is new electronic modifications.

This feature is illustrated in Figs. 2 and 3. It can be seen that in addition to the imaginary (limiting) compounds (M_4O_2, M_3O_4, M_4O_4), it is possible in the Ti–O and V–O systems to obtain a large number of phases in which the number of particles in the unit cell varies within the ranges indicated in Figs. 2 and 3. If the degree of

completeness changes under the influence of p and t along a straight line parallel to the ordinate (x = const), it follows that in the general case, as far as the limiting degree of filling of one of the sublattices, corresponding electronic modifications of the phase MO_x, which exists under ordinary experimental conditions, are realised successively. This may be followed by decomposition with the liberation of metal (for $x < 1.0$) or oxygen (for $x > 1.0$) or filling by the atoms of the "other" sublattice. In the case of compounds with vacancies in only one of the sublattices, however, filling of the unoccupied positions can take place only with a simultaneous change in composition. In other words, in order to obtain, for example, defect-free FeO it is necessary to introduce a sufficient additional quantity of iron atoms into the lattice of wüstite Fe_xO. This was demonstrated by Katsura and coworkers[65], who synthesised stoichiometric wüstite at p = 36 kbar and t = 770°.

In conclusion, other methods of realising imaginary compounds may be mentioned, for example the use of low temperatures ($t < 0$°C) and high pressures[91] and also the use of super-fast quenching from high temperatures[107]. In addition, cubic tantalum nitride has been obtained[108] by treating the metal in an atmosphere of nitrogen, ionised by a glow discharge, at $t > 1600$°. Finally, Bokii[91], following Kurnakov[83], considers that imaginary compounds can be obtained using chemical additives. This possibly applies to the cubic (NaCl type) carbide Nb_4C, synthesised by Umanskii[100]. Finally, the possibility of obtaining chemical compounds of this type by ion implantation is not excluded (see for example Ref. 109). A large number of imaginary compounds, including those predicted by Ageev[84,85], may also be realised by the methods described above, in addition to the use of high temperatures and pressures.

REFERENCES

1. P. W. Bridgman, "The Physics of High Pressure" (Translated into Russian), ONTI, Moscow–Leningrad, 1935.
2. O. I. Leipunskii, Uspekhi Khim., 8, 1519 (1939).
3. L. F. Vereshchagin and N. D. Zelinskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 443 (1943).
4. D. S. Tsiklis, Uspekhi Khim., 14, 476 (1945).
5. I. P. Krichevskii, "Fazovye Ravnovesiya v Rastvorakh pri Vysokikh Davleniyakh" (Phase Equilibria in Solutions at High Pressures), Goskhimizdat, Moscow–Leningrad, 1952.
6. B. A. Korndorf, "Tekhnika Vysokikh Davlenii v Khimii" (High Pressure Techniques in Chemistry), Gos. Izd. Khim. Lit., Moscow–Leningrad, 1952.
7. M. G. Gonikberg, Uspekhi Khim., 24, 14 (1955).
8. A. F. Kapustinskii, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 4 (1956).
9. E. V. Zubova and L. A. Korotaeva, Zhur. Fiz. Khim., 32, 1576 (1958).
10. R. Wait, Uspekhi Fiz. Nauk, 67, 705 (1959).
11. C. A. Swenson, "Physics at High Pressure" (Translated into Russian), Inostr. Lit., Moscow (1963).
12. L. F. Vereshchagin, "Kentgenostrukturnye Issledovaniya Veshchestv pri Vysokikh Davleniyakh (see Ref. 11, p. 325).
13. R. H. Wentorf (Editor), "Modern Very High Pressure Technique" (Translated into Russian), Izd. Mir, Moscow, 1964.
14. H. T. Hall and L. A. Compton, Inorg. Chem., 4, 1213 (1965).
15. L. V. Al'tshuler, Uspekhi Fiz. Nauk, 85, 197 (1965).
16. V. V. Evdokimova, Uspekhi Fiz. Nauk, 88, 93 (1966).
17. W. Paul and D. M. Warschauer (Editors), "Solids under Pressure" (Translated into Russian), Izd. Mir, 1966.
18. L. V. Al'tshuler and A. A. Bakanova, Uspekhi Fiz. Nauk, 96, 193 (1968).
19. S. M. Stishov, Uspekhi Fiz. Nauk, 96, 467 (1968).
20. A. N. Dremin and O. N. Breusov, Uspekhi Khim., 37, 897 (1968) [Russ. Chem. Rev., No. 5 (1968)].
21. K. Rumans, "Structural Studies of Various Oxides and Other Chalcogenides at Normal and High Pressures" (Translated into Russian), Izd. Mir, Moscow, 1969.
22. L. F. Vereshchagin and S. S. Kabalkina, "Strukturnye Issledovaniya Khal'kogenidov Tipa AB pri Vysokom Davlenii, Vypolnennye v SSSR" (Structural Studies of Chalcogenides of the Type AB at High Pressure, Carried Out in the USSR) (see Ref. 21, p. 176).
23. M. G. Gonikberg, Khimicheskoe Ravnovesie i Skorost' Reaktsii pri Vysokikh Davleniyakh" (Chemical Equilibrium and Reaction Rates at High Pressures), Izd. Khimiya, Moscow, 1969.
24. D. A. Kirzhnits, Uspekhi Fiz. Nauk, 104, 489 (1971).
25. N. P. Grazhdankina, Doctoral Thesis, Institute of Metal Physics, Urals Research Centre, Academy of Sciences of the USSR, Sverdlovsk, 1971.
26. L. F. Vereshchagin, E. V. Zubova, K. P. Burdina, and G. L. Aparnikov, Dokl. Akad. Nauk SSSR, 196, 817 (1971).
27. H. G. Drickamer and C. W. Frank, Ann. Rev. Phys. Chem., 23, 39 (1972).
28. Ya. A. Kalashnikov, Zhur. Vses. Khim. Obshch. im. D. I. Mendeleeva, 18, 61 (1973).
29. A. A. Zharov, Zhur. Vses. Khim. Obshch. im. D. I. Mendeleeva, 18, 73 (1973).
30. L. F. Vereshchagin, E. N. Yakovlev, G. N. Stepanov, and B. V. Vinogradov, Pis'ma v Zhur. Eksp. Teor. Fiz., 16, 382 (1973).
31. L. F. Vereshchagin, E. N. Yakovlev, B. V. Vinogradov, and V. P. Sakun, Pis'ma v Zhur. Eksp. Teor. Fiz., 20, 540 (1974).
32. O. A. Kuskov and N. I. Khitarov, Dokl. Akad. Nauk SSSR, 231, 1398 (1976).
33. D. S. Tsiklis, "Tekhnika Fiziko-khimicheskikh Issledovanii pri Vysokikh i Sverkhvysokikh Davleniyakh" (The Technique of Physicochemical Studies and High and Super-high Pressures), Izd. Khimiya, Moscow, 1976.
34. I. G. Belash, V. E. Antonov, and E. G. Ponyatovskii, Dokl. Akad. Nauk SSSR, 235, 379 (1977).
35. G. V. Samsonov, "Nitridy" (Nitrides), Izd. Naukova Dumka, Kiev, 1965.
36. B. F. Ormont, "Soedineniya Peremennogo Sostava" (Compounds of Variable Composition), Izd. Khimiya, Leningrad, 1969.
37. L. E. Toth, "Transition Metal Carbides and Nitrides" (Translated into Russian), Izd. Mir, Moscow, 1974.
38. G. V. Samsonov, G. Sh. Upadkhaya, and V. S. Neshpor, "Fizicheskoe Materialovedenie Karbidov" (The Physical Examination of Carbides), Izd. Naukova Dumka, Kiev, 1974.
39. P. M. Ogibalov and I. A. Kiiko, "Povedenie Veshchestva pod Davleniem" (The Behaviour of Substances Under Pressure), Izd. Moskov. Gos. Univ., 1962, p. 21.

40. P.W. Bridgman, "Recent Work in the Field of High Pressure" (Translated into Russian), Inostr. Lit., Moscow, 1948, pp. 63, 100, 178.
41. A.A. Semerchan, M.L. Baskin, and L. Kh. Pivovarov, Fiz. Metallov i Metalloved., 15, 941 (1963).
42. L.F. Vereshchagin, V.A. Galaktionov, A.A. Semerchan, and V.N. Slesarev, Dokl. Akad. Nauk SSSR, 132, 1959 (1960).
43. L. Kh. Pivovarov, S.I. Yanshin, A.A. Se rchan, and M.L. Baskin, Fiz. Metallov i Metalloved., 17, 606 (1964).
44. A.E. Koval'skii, A.I. Prikhna, E.A. Rybakova, I.I. Timofeeva, and A.A. Shul'zhenko, Izv. Akad. Nauk SSSR, Metally, No. 4, 231 (1968).
45. G.V. Samsonov, V.I. Kovtun, I.I. Timofeeva, A.V. Bochko, S.S. Dzhafarov, and V.S. Polishchuk, in collected papers "Vliyanie Vysokikh Davlenii na Veshchestvo" (Collected Papers on the Influence of High Pressures on Materials), ONTI IPM VN Ukrain. SSR, Kiev, 1976, p. 169.
46. G.V. Samsonov, I.I. Timofeeva, V.I. Kovtun, V.P. Alekseevskii, Yu.A. Litvin, and V.V. Yarosh, in collected papers "Vliyanie Vysokikh Davlenii na Veshchestvo" (Collected Papers on the Influence of High Pressures on Materials), ONTI IPM VN Ukrain. SSR, Kiev, 1976, p. 9.
47. E. Rudy and J.R. Hoffman, Planseeber. f. Pulvermet., 15, 174 (1967).
48. L.G. Sevast'yanova, Yu.A. Velikodnyi, E.V. Zubova, L.M. Kovba, V.M. Krutskikh, and N.A. Kudrya, Dokl. Akad. Nauk SSSR, 229, 357 (1976).
49. E.V. Clougherty, K.H. Lothrop, and J.A. Kafalas, Nature, 191, No. 4794, 86 (1961).
50. H. Nowotny, E. Parthe, R. Kieffer, and F. Benesovsky, Monatsh. Chem., 85, 255 (1954).
51. E. Rudy, S. Windisch, A.J. Stosick, and J.R. Hoffman, Trans. AIME, 239, 1247 (1967).
52. A.Ya. Shinyaev, V.B. Fedorov, L.V. Gorshkova, and D.B. Chernov, Dokl. Akad. Nauk SSSR, 212, 1336 (1973).
53. L.B. Dubrovskaya and S.Z. Nazarova, Zhur. Eksp. Teor. Fiz., 68, 238 (1975).
54. S.S. Batsanov, "Doklady I Vsesoyuznogo Simpoziuma po Impul'snym Davleniyam" (Papers Presented at the First All Union Symposium on Pressure Pulses), Vol. 2, Izd. VNIIFTRI, Moscow, 1974, p. 4.
55. G.A. Adadurov, O.N. Breusov, A.N. Dremin, and V.F. Tatsii, Poroshkovaya Metallurgiya, No. 11, 7 (1971).
56. E.V. Chagelishvili, Fiz. Goreniya i Vzryva, 7, 275 (1971).
57. G.V. Samsonov, V.P. Alekseevskii, S.A. Bozhko, and V.V. Yarosh, Poroshkovaya Metallurgiya, No. 1, 93 (1972).
58. A.V. Anan'in, O.N. Breusov, A.N. Dremin, S.V. Pershin, V.F. Tatsii, and F.A. Fekhretdinov, Poroshkovaya Metallurgiya, No. 10, 100 (1974).
59. G.V. Samsonov, I.I. Timofeeva, V.I. Kovtun, V.P. Alekseevskii, V.V. Yarosh, and V.S. Polishchuk, in collected papers "Vliyanie Vysokikh Davlenii na Veshchestvo" (Collected Papers on the Influence of High Pressure on Materials), Kiev, 1976, p. 15.
60. G.A. Adadurov, O.N. Breusov, A.N. Dremin, and V.N. Drobyshev, Poroshkovaya Metallurgiya, No. 3, 71 (1971).
61. L.G. Boiko and S.V. Popova, Pis'ma v Zhur. Eksp. Teor. Fiz., 12, 101 (1970).
62. G.V. Samsonov, V.P. Alekseevskii, Yu.N. Beletskii, V.M. Pan, I.I. Timofeeva, L.K. Shvedova, and V.V. Yarosh, in collected papers "Issledovanie Nitridov" (Collected Papers on the Study of Nitrides), Kiev, 1975, p. 219.
63. V.M. Volkogon, Yu.I. Sozin, A.V. Belyanki , V.I. Vityuk, and E.S. Cherepenina, in collected papers "Vliyanie Vysokikh Davlenii na Veshchestvo" (Collected Papers on the Influence of High Pressure on Materials), Kiev, 1976, p. 55.
64. V.I. Arkharov and D.K. Bulychev, Dokl. Akad. Nauk SSSR, 113, 791 (1957).
65. T. Katsura, B. Iwasaki, S. Kimura, and S. Akimoto, J. Chem. Phys., 47, 4559 (1967).
66. N.J. Doyle, J.K. Hulm, C.K. Jones, R.C. Miller, and A. Taylor, Phys. Letters, 26A, 604 (1968).
67. A. Taylor and N.J. Doyle, Colloq. Intern. Centre Nation. Rech. Scient., No. 188, 261 (1970).
68. H. Iwasaki, K. Asaumi, K. Kamigaki, S. Ogawa, O. Terasaki, and D. Watanabe, J. Phys. Soc. Japan, 30, 180 (1971).
69. R.L. Clendenen and H.G. Drickamer, J. Chem. Phys., 44, 4223 (1966).
70. H. Iwasaki, J. Appl. Phys. Japan, 10, 1149 (1971).
71. M.D. Banus, T.B. Reed, and A.J. Strauss, Phys. Rev. *B*; Solid Stat., 5, 2775 (1975).
72. Yu.G. Zainulin, S.I. Alyamovskii, G.P. Shveikin, S.V. Popova, and L.G. Boiko, Fiz. Tverd. Tela, 19, 858 (1977).
73. N.A. Bendeliani, S.V. Popova, and L.F. Vereshchagin, Geokhimiya, 5, 499 (1966).
74. P. Ehrlich, Z. Elektrochem., 45, 362 (1939).
75. M.E. Straumanis, T. Ejima, and W.J. James, Acta crystallogr., 14, 493 (1961).
76. E.D. Ruchkin, A.E. Strelyaev, V.A. Litvinova, E.V. Lazareva, and S.S. Batsanov, Zhur. Neorg. Khim., 18, 2855 (1973) [Russ. J. Inorg. Chem., No. 10 (1973)].
77. Y. Syono, T. Goto, J. Nakai, Y. Nakagawa, and H. Iwasaki, J. Phys. Soc. Japan, 37, 442 (1974).
78. M.D. Banus and T.B. Reed, Chemistry of Extended Defects in Non-metallic Solids, North-Holland, Amsterdam, 1970, p. 488.
79. N.A. Toropov, V.P. Barzakovskii, I.A. Bondar', and Yu. P. Udalov, "Diagrammy Sostoyaniya Silikatnykh Sistem. Spravochnik" (Reference Book of Equilibrium Diagrams of Silicate Systems), Vol. 2, Izd. Nauka, Leningrad, 1970, pp. 181, 237.
80. Yu.G. Zainulin, S.I. Alyamovskii, and S.V. Popova, Zhur. Neorg. Khim., 23, 1155 (1978) [Russ. J. Inorg. Chem., No. 5 (1978)].
81. L.F. Vereshchagin, L.G. Khvostantsev, A.P. Novikov. A.V. Kvin, V.I. Veprentsev, L.I. Klyachko, A.S. Novgorodov, V.M. Zubkov, and S.A. Yanshin, B.P. 1342369 (1971); Byul. Izobretenii za Rubezhom, Part 4, No. 1, 17 (1974).
82. Yu.G. Zainulin, S.I. Alyamovskii, G.P. Shveikin, and S.V. Popova, Dokl. Akad. Nauk SSSR, 234, 358 (1977).
83. N.S. Kurnakov, "Vvedenie v Fiziko-khimicheskii Analiz" (Introduction to Physicochemical Analysis), Izd. Akad. Nauk SSR, Moscow–Leningrad, 1940, p. 126.
84. N.V. Ageev, Izv. Akad. Nauk SSSR, Ser. Khim., 285 (1936).
85. N.V. Ageev, "Khimiya Metallicheskikh Splavov" (The Chemistry of Metallic Alloys), Izd. Akad. Nauk SSSR, 1941, p. 67.

86. S. A. Shchukarev, Vestnik Leningrad. Gos. Univ., No. 5, 5 (1947).
87. V. I. Mikheeva, Izv. Sektora Fiz. -Khim. Anal. Inst. Obschch. Neorg. Khim. Akad. Nauk SSSR, 17, 174 (1949).
88. E. S. Makarov, Zhur. Neorg. Khim., 1, 583, 2032 (1956).
89. B. F. Ormont, Zhur. Neorg. Khim., 1, 1457 (1956).
90. "Rezolyutsiya III Vsesoyuznogo Soveshchaniya po Fiziko-khimicheskomu Analizu po Opredeleniyu Ponyatiya Khimicheskogo Soedineniya" (Resolution of the Third All Union Conference on Physicochemical Analysis, on the Definition of the Concept of Chemical Compound), Zhur. Neorg. Khim., 1, 1597 (1956).
91. G. B. Bokii, Zhur. Neorg. Khim., 1, 1159, 1599 (1956); 8, 1041 (1963) [Russ. J. Inorg. Chem., No. 5 (1963)]; Zhur. Strukt. Khim., 4, 73 (1963).
92. V. I. Kuznetsov, "Evolyutsiya Predstavlenii ob Osnovnykh Zakonakh Khimii" (The Evolution of the Ideas of the Basic Laws of Chemistry), Izd. Nauka, Moscow, 1967, p. 77.
93. B. F. Ormont, "Soedineniya Peremennogo Sostava" (Compounds of Variable Composition), Izd. Khimiya, Leningrad, 1969, Chapters I and II.
94. E. S. Makarov, "Izomorfizm Atomov v Kristallakh" (Isomorphism of Atoms in Crystals), Atomizdat, Moscow, 1973, p. 47.
95. V. Ya. Anosov, N. I. Ozerova, and Yu. Ya. Fialkov, "Osnovy Fiziko-kh' 'icheskogo Analiza" (Principles of Physicochemical Analysis), Izd. Nauka, Moscow, 1976, Chapters III and XI.
96. V. I. Mikheeva, "Metod Fiziko-khimicheskogo Analiza v Neorganicheskom Sinteze" (Physicochemical Analysis in Inorganic Synthesis), Izd. Nauka, Moscow, 1977, Chapter I.
97. Yu. G. Zainulin, S. I. Alyamovskii, and G. P. Shveikin, Zhur. Neorg. Khim., 22, 2307 (1977) [Russ. J. Inorg. Chem., No. 8 (1977)].
98. S. V. Popova and L. G. Boiko, High Temperat. -High Pressures, 3, 237 (1971).
99. S. V. Popova, L. N. Fomicheva, and L. G. Khvostantsev, Pis'ma v Zhur. Eksp. Teor. Fiz., 16, 609 (1972).
100. Ya. S. Umanskii, Zhur. Fiz. Khim., 14, 332 (1940).
101. E. K. Storms, "Refractory Carbides" (Translated into Russian), Atomizdat, Moscow, 1970, p. 17.
102. P. Ehrlich, Z. anorg. allgem. Chem., 259, 1 (1949).
103. E. Rudy and F. Benesovsky, Monatsh. Chem., 92, 432 (1961).
104. V. A. Tskhai, Summary of Doctoral Thesis, IPM, Akad. Nauk Ukrain. SSR, Kiev, 1973.
105. G. P. Shveikin, A. L. Ivanovskii, V. A. Gubanov, E. Z. Kurmaev, S. A. Trofimova, Yu. G. Zainulin, S. I. Alyamovskii, and S. V. Popova, Dokl. Akad. Nauk SSSR, 246, 413 (1978).
106. B. E. Gokhshtein, P. O. Pashkov, and I. I. Polyakova, in collected papers "Metallovedenie i Prochnost' Materialov" (Collected Papers on Metal Science and the Strength of Materials), Vol. 1, Volgograd, 1968, p. 199.
107. E. M. Savitskii, Yu. V. Efimov, and T. M. Frolova, Dokl. Akad. Nauk SSSR, 236, 581 (1977).
108. A. A. Babad-Zakhryapin, M. I. Lagutkin, and L. G. Yushina, Izv. Akad. Nauk SSSR, Neorg. Materialy, 12, 1130 (1976).
109. G. V. Afanas'ev, I. G. Gverdtsiteli, A. I. Guldamashvili, E. M. Diasamidze, A. N. Kalinin, I. K. Karpenko, and N. M. Kutsiya, Kristallografiya, 22, 841 (1977).

Institute of Chemistry,
Sverdlovsk