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Magnetic susceptibility of nonstoichiometric compounds of transition d-metals

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Contents

Abstract. Results of research on the magnetic susceptibility of nonstoichiometric compounds of group IV and V transition d-metals are generalized. It is shown that nonstoichiometry-related susceptibility changes in transition metal carbides are associated with the peculiarities of the electron energy spectra in carbides. The immediate cause for the reduced susceptibility of nonstoichiometric carbides during atomic-vacancy ordering is the change in the contribution from orbital paramagnetism, due to short-range ordering. A possibility to employ the magnetic susceptibility for estimating short- and long-range order parameters and determining the superstructure type in nonstoichiometric compounds is discussed.

1. Introduction

Cubic (with a *B*1 structure) carbides, nitrides, and oxides MX_y ($M =$ Ti, Zr, Hf, V, Nb, Ta; $X =$ C, N, O) belong to the group of strongly nonstoichiometric compounds [1, 2]. The cubic carbides $M\mathrm{C}_y$ and nitrides $M\mathrm{N}_y$ ($y < 1$) of such transition metals as Ti, Zr, Hf, V, Nb, and Ta possess high electronic conduction and high heat conduction and are paramagnets, i.e., retain some of the properties characteristic of metals. To a lesser degree, this is true of cubic monoxides TiO_y and VO_y. In titanium monoxide, the conduction in the homogeneity region of the cubic phase varies from the electronic type, typical of metals, to the np-type, typical of semiconductors, while vanadium monoxide is a semiconductor, independent of its composition. The formation of carbides, nitrides, and oxides with a *B*1 structure is accompanied not only by changes in the crystal structure of the metal (the hexagonal close-packed, or hcp, lattice of Ti, Zr, and Hf, and the body-centered lattice of V, Nb, and Ta are replaced by the face-centered cubic, or fcc, metal sublattice in carbides) but also by significant changes in the electron energy spectrum and an overall decrease in the electronic density. What makes the crystal structure of nonstoichiometric compounds with a *B*1 structure so specific is the location of the nonmetal interstitial atoms (C, N, and O) at the octahedral interstitial sites of the fcc metal sublattice, with the interstitial atoms capable of occupying all interstitial sites or a certain fraction of them. The concentration of vacant interstitial sites (the structural vacancies □) may vary within broad limits from 0 to 30 – 50 at.% and determine the high nonstoichiometry of cubic compounds MX_y and the presence in them of wide homogeneity regions [1, 2].

The high concentration of structural vacancies is the most important property of strongly nonstoichiometric carbides. Depending on the existing external conditions, carbon atoms and structural vacancies may be distributed among the sites of the nonmetallic sublattice statistically (in a disordered manner) or with a certain degree of short- and long-range order. A disordered distribution appears as thermodynamically equilibrium at high temperatures (higher than 1300 – 1400 K), while at low temperatures the ordered distribution shows itself as equilibrium. At the same time, a disordered state may easily be retained at low temperatures as a result of quenching of the nonstoichiometric carbides against a high temperature. At 300 K, a disordered state of strongly nonstoichiometric carbides is quite stable and may exist for an infinitely long time as a metastable state. The effect of concentration and the nature of the vacancy distribution on the structure and properties of nonstoichiometric compounds is substantial [1, 2].

By establishing the dependence of the properties of nonstoichiometric compounds not only on the composition but also on the degree of order in the distribution of atoms and vacancies in the crystal lattice we acquire additional possibilities for the controlled synthesis of materials with

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given and precisely controllable properties and discover new areas of their practical applications.

For a long time, various methods of X-ray diffraction analysis were used for determining the position of interstitial atoms in the lattice of nonstoichiometric compounds. However, the small amplitudes for X-ray scattering by the interstitial atoms compared with the amplitudes for scattering by metal atoms do not always make it possible to determine the position of the interstitial atoms by analyzing the intensities of the diffraction lines. The development of experimental techniques and especially the use of neutron diffraction analysis for studying the crystal structure of nonstoichiometric compounds revealed that under certain conditions an ordered distribution of interstitial atoms may be observed. Structural neutron diffractometry is one of the most informative methods for studying nonstoichiometric compounds, because the intensity of neutron scattering by the nuclei of low-Z atoms is comparable to the intensity of scattering by transition-metal atoms. The ordering of interstitial atoms in these compounds was also discovered by such a diffraction method as electron diffractometry.

However, it is not always possible to study the structure of ordered nonstoichiometric carbides by diffraction methods. For instance, in the case of tantalum and hafnium carbides, the relative intensity of superstructure reflections in an X-ray experiment is extremely low due to the large difference in the amplitudes of scattering by metal atoms, on the one hand, and carbon atoms, on the other. The diffraction of neutrons in the TaC_y and HfC_y carbides also provides little information, since, owing to the very high absorption of neutrons by the massive nuclei of metals, the overall intensity of the diffraction spectrum is low and there is practically no way that the superstructure reflections and small-angle short-range order effects can be observed by such methods.

An accepted method for studying the structure and the short-range order is the nuclear magnetic resonance (NMR) spectroscopy. However, the possibilities presented by the NMR method for studying the atomic distributions in the crystal lattices of carbides, nitrides, and oxides of transition metals are also limited. NMR studies of the VC_y and NbC_y carbides are possible basically (and have been realized in practice) since the nuclei of the most abundant ^{51}V and ^{93}Nb isotopes have magnetic moments. So far there have been no NMR studies of tantalum compounds that have involved ^{181}Ta nuclei. It is practically impossible to apply the NMR method to studies of the nonstoichiometric carbides TiC_y, ZrC_y, and HfC_y, since the most abundant ^{48}Ti, ^{46}Ti, ^{92}Zr, ^{94}Zr, ^{180}Hf, ^{176}Hf, and ^{174}Hf isotopes have nuclei with spin zero, which therefore possess no magnetic moment. Theoretically, NMR can be used when the ^{49}Ti, ^{91}Zr, and ^{179}Hf isotopes are utilized, but we know of no such research. Finally, NMR studies of the structure of nonstoichiometric carbides may be carried out using the nuclei of the ^{13}C isotope with spin $1/2$, but such studies have yet to be conducted. An investigation of the magnetic resonance of the ^{14}N nuclei in nonstoichiometric nitrides has not been carried out either.

Since the application of direct structural methods to studies of the structure of disordered and ordered nonstoichiometric carbides, nitrides, and oxides is not always possible, a group of researchers from Russia (A A Rempel', V N Lipatnikov, S Z Nazarova, and others) pioneered in proposing and actually realizing an indirect method of studying short- and long-range order by measuring magnetic susceptibility.

Magnetic susceptibility is one of the few properties of crystalline substances that is determined solely by the electron subsystem and is independent of the of the phonon energy spectrum. Hence, the investigation of the susceptibility of ordered and disordered phases of nonstoichiometric compounds makes it possible to get an idea not only of the degree of order but also of changes in the electronic structure caused by deviations from stoichiometry and by formation of a superstructure.

Until recently, the scientific literature contained no information not only about studies of how to use magnetic susceptibility when investigating the structure of nonstoichiometric compounds in states with different degrees of order, but even about the nonstoichiometry effect on the susceptibilities of such compounds. There are two objective reasons for this. The first (and apparently the most important) one is the complexity of the synthesis of such compounds with proper certification of composition and structure. The absence of easily available objects of research has led to a deficit in scientific information about such objects. Only in the last 25 to 30 years of the 20th century did several groups of researchers in the USSR, France, Great Britain, Austria, Japan, and the US achieve certain progress in studying and understanding the structure of strongly nonstoichiometric compounds. These results have been generalized in monographs (see Refs [1, 2]) and in reviews [3, 4] dealing with phase equilibria in systems with nonstoichiometry and atomic-vacancy ordering. As for the magnetic susceptibility of the compounds in question, the effect that nonstoichiometry and ordering has on it in the niobium NbC_y and tantalum TaC_y carbides, has been briefly discussed in the review [5] devoted to the influence of atomic-vacancy ordering on the various properties of nonstoichiometric carbides. The possibility of employing temperature measurements of the magnetic susceptibility to analyze the short-range order in nonstoichiometric carbides was also discussed in Ref. [6]. Galoshina discussed in her review article [7] the magnetic susceptibility of transition metals in connection with their electronic structure.

Since magnetic susceptibility χ of strongly nonstoichiometric compounds is very similar to the magnetic susceptibility of transition metals, we will now discuss very briefly the features of the susceptibility of such metals.

Figure 1 displays the temperature dependences of the magnetic susceptibility $\chi(T)$ for titanium, zirconium, hafnium, vanadium, niobium, and tantalum, which form strongly nonstoichiometric MC_y carbides with the cubic structure $B1$. Clearly, the results of different researchers [8–16] agree fairly well. In each period, both the mass (per gram) and atomic (per 1 g-at.) susceptibilities of metals with an odd number of $(n+1)$s- and nd-electrons (V, Nb, and Ta with five s- and d-electrons) are higher than the susceptibility of metals with an even number of s- and d-electrons (Ti, Zr, and Hf with four s- and d-electrons), i.e., $\chi_{V} > \chi_{Ti}$, $\chi_{Nb} > \chi_{Zr}$, and $\chi_{Ta} > \chi_{Hf}$. In each group, the mass and atomic susceptibilities decrease as the number of electrons in filled electron shells (the ion core) increases: $\chi_{Ti} > \chi_{Zr} > \chi_{Hf}$, $\chi_{V} > \chi_{Nb} > \chi_{Ta}$. As the temperature grows, the magnetic susceptibility χ of titanium, zirconium, and hafnium increases, but that of vanadium, niobium, and tantalum decreases (see Fig. 1); a discontinuity in the susceptibility of Ti, Zr, and Hf at roughly 1150 K is related to a polymorphic phase transition of the metals from the hcp structure to the body-centered cubic (bcc) structure.

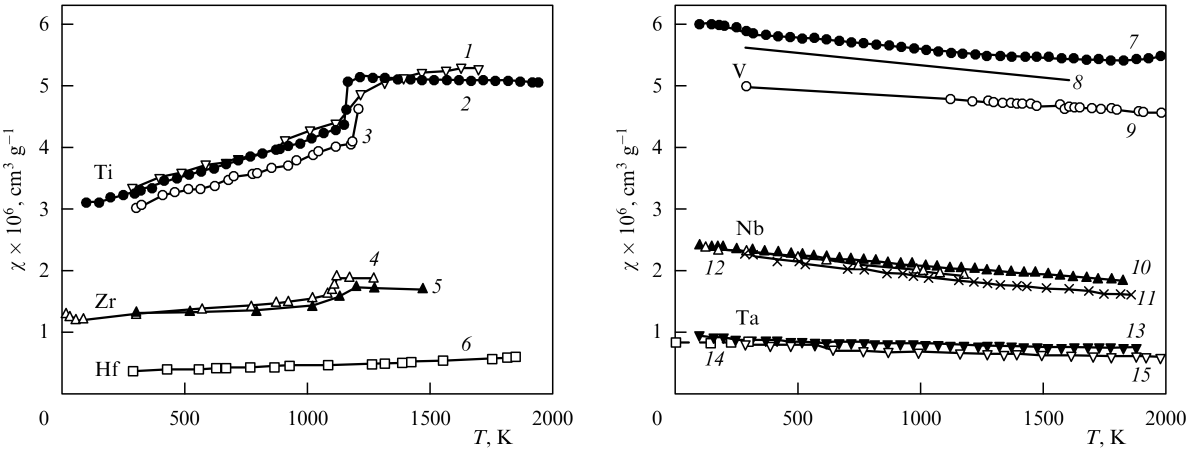

Figure 1. Magnetic susceptibility of group IV and V transition d-metals: Ti — *1* [8], *2* [9], and *3* [10]; Zr — *4* [11] and *5* [12]; Hf — *6* [8]; V — *7* [9], *8* [12], and *9* [13]; Nb — *10* [14], *11* [8], and *12* [15], and Ta — *13* [14], *14* [16], and *15* [8].

The size and behavior of the magnetic susceptibility of the metals in question are determined by the band structure of the metals, primarily by the position and density of electronic states at the Fermi level, $N(E_F)$. In transition metals, thanks to the close proximity of the energies of the nd- and $(n+1)$s-levels, the unfilled s- and d-bands overlap, with the density of states in the d-band being much higher than in the s-band, while the Fermi level is located below the upper edge of the d-band. This explains the fairly large value of $N(E_F)$ and, as a result, the higher magnetic susceptibility of transition metals compared with that of normal metals. Indeed, an essential positive contribution to susceptibility is supplied by Pauli's paramagnetism of the conduction electrons, which is proportional to the density $N(E_F)$ of electronic states at the Fermi level:

$$\chi_p^- = 2\mu_B^2 N(E_F)\,, \tag{1}$$

where μ_B is the Bohr magneton. The magnitude of the density of electronic states at the Fermi level, with allowance for its renormalization because of electron–phonon interaction, is in turn proportional to the electronic specific heat coefficient γ, namely

$$N(E_F) = \frac{3\gamma}{\pi^2 k_B^2 N_A (1+\lambda)}\,, \tag{2}$$

where λ is the electron–phonon coupling constant, k_B is the Boltzmann constant, and N_A is the Avogadro constant. Table 1 lists the values of γ and λ for Ti, Zr, Hf, V, Nb, and Ta according to the data of works [7, 17–31], and also the values of the density of states at the Fermi level, $N(E_F)$, determined from the data on electronic specific heat [31–35] and band calculations [33]. In group V metals, the Fermi level lies near the maximum of the density-of-states curve $N(E)$, while in group IV metals it lies near the minimum, with the result that, as Table 1 suggests, in group V metals the density of electronic states at the Fermi level, $N(E_F)$, is higher than the density of electronic states in group IV metals. In view of this, the magnetic susceptibility in each period increases as we move from group IV metals to group V metals. The shape of the density-of-states curve and the position of the Fermi level in it also determine the sign of the temperature coefficient of susceptibility, $d\chi/dT$: near the maximum and minimum of the density-of-states curve, the sign of $d\chi/dT$ coincides with that of the second energy derivative $(d^2N(E)/dE^2)_{E=E_F}$ of the density of states at $E = E_F$. In group IV metals, the Fermi level lies near the minimum of the density of states, where $(d^2N(E)/dE^2)_{E=E_F} > 0$, while in group V metals it lies near the maximum, where $(d^2N(E)/dE^2)_{E=E_F} < 0$, in view of which the coefficient $d\chi/dT$ for titanium, zirconium, and hafnium is positive, while for vanadium, niobium, and tantalum it is negative (see Fig. 1).

The negative contribution to the susceptibility is provided by the diamagnetism of the ion cores, χ_d^+, and the absolute value of this contribution in each group increases with the number of electrons in the ion core; the value of χ_d^+ for Ti^{4+}, Zr^{4+}, and Hf^{4+} measures -5×10^{-6}, -10×10^{-6}, and -16×10^{-6} cm^3 g-at.$^{-1}$, respectively, while for V^{5+}, Nb^{5+}, and Ta^{5+} it equals -4×10^{-6}, -9×10^{-6}, and -14×10^{-6} cm^3 g-at.$^{-1}$, respectively [52]. The contribution of core diamagnetism determines the decreases in the magnetic susceptibility χ in each group of transition metals, as we go from titanium to hafnium or from vanadium to tantalum.

Note that polycrystalline samples were used to obtain the $\chi(T)$ curves in Fig. 1 for transition metals. Group V metals with a bcc structure are isotropic and their susceptibility does not depend on how the magnetic field is directed in relation to the crystallographic axes. As for the group IV transition metals, which possess an hcp structure, anisotropy of magnetic susceptibility has been detected in their single crystals [10, 19, 20, 53, 54].

Comparison of the $\chi(T)$ curves of transition metals and their carbides with a composition that is closest to the stoichiometric one shows that the mutual 'arrangement' of carbides in relation to the value of χ is the same as for proper metals, but that the carbides feature a lower susceptibility (Figs 2 and 3). No cubic vanadium carbide of stoichiometric composition exists, in contrast to carbides of other transition metals; the upper boundary of the homogeneity region for the compound is formed by the $VC_{0.88}$ carbide, whose susceptibility is shown in Fig. 3. The smaller absolute value of the carbide susceptibility is caused, first, by their lower electron density compared with that of the metals, since in carbides a number of d-electrons of the metal form covalent M–C bonds with 2p-electrons of the carbon atoms [1, 2, 62, 63]. Table 1 clearly shows that the electronic specific heat coefficient γ and the density of electronic states at the Fermi

Table 1. Electronic specific heat coefficient γ, electron – phonon coupling constant λ, and density of electronic states $N(E_F)$ at the Fermi level for transition d-metals M and their cubic carbides MC_y, zirconium nitride ZrN_y, and titanium monoxide TiO_y.

Metal M	γ, mJ g-at.$^{-1}$ K^{-2}	λ	$N(E_F)$, eV^{-1} atom^{-1}	Compound MX_y	γ, mJ mol^{-1} K^{-2}	λ	$N(E_F)$, eV^{-1} form. u.$^{-1}$
α-Ti	3.56 [17][1]	0.38 [30]	0.76 [32]	TiC	0.51 [36, 37]	—	0.23 [46]
	3.32 [18]	0.19 [19]	0.96 [33][2]	$TiC_{0.90}$	1.29 [37]		
	3.36 [19, 20]		1.03 [33][3]	$TiC_{0.50}$			0.43 [38][2]
				$TiC_{1.00}$			0.10 [38][2]
				$TiO_{0.96}$[4]	2.92 [39]	0.37 [39]	0.90 [39][5]
				$TiO_{1,00}$[4]	2.46 [39]	0.37 [39]	0.76 [39][5]
				$TiO_{1.06}$[4]	3.06 [39]	0.37 [39]	0.95 [39][5]
				$TiO_{1.00}$			0.75 [40][2]
				$TiO_{1.00}$			0.29 [41][2], 0.61 [42][2]
				$TiO_{1.00}$			0.25 [43][2]
α-Zr	3.04 [17]	0.41 [30]	0.96 [33][2]	ZrC	0.75 [44]		
	2.80 [20]	0.20 [20]	0.84 [33][3]	$ZrC_{0.60}$			0.33 [45][2]
	2.75 [21]			$ZrC_{1.00}$			0.09 [45][2]
	2.81 [22, 23]		0.60 [34]				
				$ZrN_{0.65}$			0.32 [45][2]
				$ZrN_{1.00}$			0.15 [45][2]
α-Hf	2.64 [17]	0.34 [30]	0.73 [33][2]	HfC	0.75 [44]		
	2.16 [23]		0.57 [35]				
	2.15 [20, 24]	0.17 [20]	0.68 [33][3]				
V	9.9 [18]			$VC_{0.90}$	3.03 [37]		
	9.26 [25]			$VC_{0.875}$	3.18 [46]		0.67 [46][6]
	8.88 [26][1]		1.61 [32]	$VC_{0.65}$	3.38 [46]		0.72 [46][6]
				$VC_{0.70}$			0.30 [38][2]
				$VC_{0.875}$			0.32 [38][2]
Nb	7.8 [27]	—	2.18 [34]	$NbC_{0.77}$	2.11 [47]	—	—
	7.74 [28, 29]	0.82 [31][7]	1.81 [31]	$NbC_{0.83}$	2.82 [48][8]	0.48 [48]	0.73 [48][8]
				$NbC_{0.96}$	2.83 [47]	—	—
				$NbC_{0.98}$	5.25 [31, 49][8]	0.74 [31, 49]	1.27 [31, 49][8]
				$NbC_{0.73}$			0.24 [45][2]
				$NbC_{0.83}$			0.17 [45][2]
				$NbC_{1.00}$			0.19 [45][2]
				$NbC_{0.70}$			0.21 [50][2]
				$NbC_{0.85}$			0.17 [50][2]
				$NbC_{1.00}$			0.22 [50][2]
Ta	5.85 [28, 29]	0.65 [31][7]	1.51 [31]	TaC	3.2 [36]	—	1.44 [36]
	5.9 [7]		2.52 [35][9]	$TaC_{0.78}$	2.05 [47]	—	
				$TaC_{0.95}$	2.87 [47]	—	
				$TaC_{0.99}$	6.21 [31, 49][8]	0.82 [31, 49]	1.45 [31, 49][8]

[1] The electronic specific heat coefficient γ was calculated in Ref. [32] on the basis of the experimental data obtained in the works cited.

[2] Band calculation.

[3] Calculated in Ref. [33] on the basis of the data on the coefficient γ taken from Refs [19, 20]; the values of λ were taken from Ref. [30].

[4] The low-temperature specific heat was measured by Okaz and Keesom [39] in fused samples of TiC_y in the form of tablets with a round upper edge; for cylindrical $TiO_{0.91}$, $TiO_{0.95}$, $TiO_{1.00}$, and $TiO_{1.17}$ samples 4 mm in diameter and 40-mm long, the average value of the electron – phonon coupling constant λ was 0.37, the coefficient γ was 3.54, 3.33, 3.16, and 4.50 mJ mol^{-1} K^{-2}, respectively, and the value of $N(E_F)$ amounted to 1.00, 1.03, 0.98, and 1.39 eV^{-1} per formula unit. The molar heat capacity of the monoxide TiO_y (Ti_xO_z, where $y = z/x$) was obtained by Okaz and Keesom [39] without allowance for defects in the titanium sublattice, with the result that its values and those of γ are overestimated.

[5] In the original paper by Okaz and Keesom [39], $N(E_F)$ was calculated directly from the molar electronic heat capacity coefficient, i.e., in units [eV^{-1} form.u.$^{-1}$], but by mistake the unit [eV^{-1} atom^{-1}] was indicated.

[6] Calculated from the electronic specific heat coefficient.

[7] The electron – phonon coupling constant λ was calculated in Ref. [31] on the basis of the experimental data taken from Refs [28, 29, 51].

[8] In Refs [31, 48, 49], the coefficient γ and the density of electronic states $N(E_F)$ of the carbides MC_y ($NbC_{0.83}$, $NbC_{0.98}$, and $TaC_{0.99}$) are measured in the units [mJ g-at.$^{-1}$ K^{-2}] and [eV^{-1} atom^{-1}], respectively; here, these values are given per mole and per formula unit, respectively, i.e., they have been obtained by multiplying γ and $N(E_F)$ by $(1 + y)$.

[9] In Ref. [35], the value of the density of spin states is half the one listed here: $N_{sp}(E_F) = N(E_F)/2$.

level, $N(E_F)$, in carbides are also smaller than in the respective metals, in view of which the paramagnetic Pauli component of the carbide susceptibility turns out to be smaller than the respective component in transition metals. Indeed, the electron energy spectra of carbides differ substantially from those of the corresponding transition metals. As an example, in Fig. 4 we display the calculated density of electronic states $N(E)$ for metallic α-Ti with the hcp structure [33] and the stoichiometric titanium carbide $TiC_{1.0}$ [64]. The band of the valence electrons of titanium carbide, in contrast to that of metallic titanium, consists of three bands: the low-energy 2s(C)-band containing the small contributions from s-, p-,

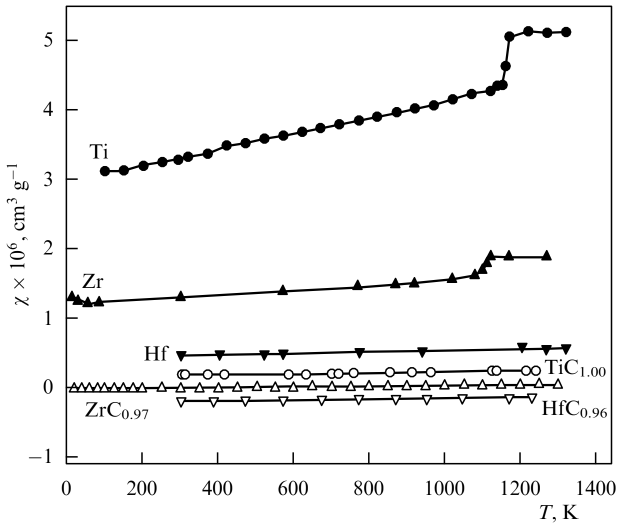

Figure 2. Comparison of magnetic susceptibilities $\chi(T)$ of group IV transition d-metals and their MC_y carbides that are close in composition to the stoichiometric compounds: Ti [9], $TiC_{1.00}$ [55], Zr [11], $ZrC_{0.97}$ [56], Hf [8], and $HfC_{0.96}$ [57].

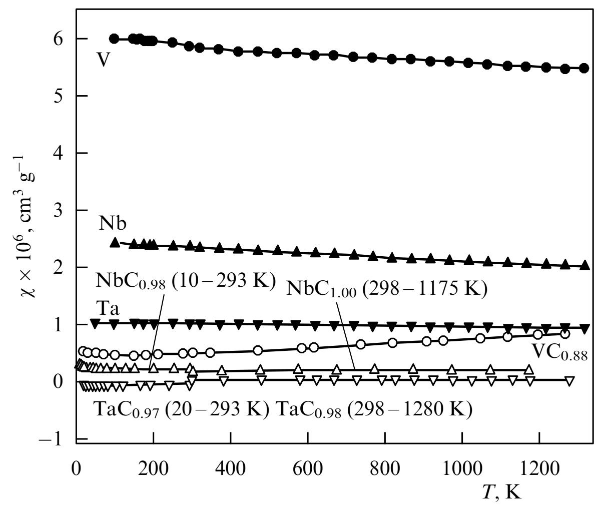

Figure 3. Comparison of magnetic susceptibilities $\chi(T)$ of group V transition d-metals and their MC_y carbides: V [9], $VC_{0.88}$ [58], Nb [14], $NbC_{0.98}$ [59], $NbC_{1.00}$ [60], Ta [14], $TaC_{0.97}$ [59], and $TaC_{0.98}$ [61].

and d-states of the metal; the main valence-coupling band formed by the strong mixing of the 2p(C)- and d(Ti)-wave functions, and the high-energy partially filled conduction band moulded primarily by the d(M)-functions with an admixture of 2p(C)-, p(M)-, and s(M)-functions. The redistribution of individual atomic states in a carbide leads to a partial transfer of charge between the atoms of the metal and carbon, which generates the ionic constituent of the chemical bond. Thus, in titanium carbide, as in all cubic carbides MC and nitrides MN of the transition metals, a combined covalent – metal – ionic type of the chemical bond is realized [1, 2, 62, 63]. The Fermi level in titanium and titanium carbide lies at the minimum of the density-of-states curve, but the density of electronic states at the Fermi level in metallic titanium is much higher than $N(E_F)$ of titanium carbide.

The sign of the temperature coefficient of magnetic susceptibility for the MC_y carbides of group IV transition metals is the same as for the corresponding transition metals Ti, Zr, and Hf (see Fig. 2). For carbides of group V transition metals that are close in composition to the stoichiometric compound $M^{(V)}C_{1.0}$, the temperature coefficient $d\chi/dT \leqslant 0$, which coincides with the negative sign of $d\chi/dT$ for the transition metals Nb and Ta (see Fig. 3). For the nonstoichiometric $M^{(V)}C_y$ carbides of vanadium, niobium, and tantalum, the temperature coefficient $d\chi/dT$ is positive. The change in the sign of $d\chi/dT$ is caused by the high content of carbon vacancies, which leads to substantial modification of the band structure of the nonstoichiometric carbides $M^{(V)}C_y$ compared with that of the stoichiometric $M^{(V)}C_{1.0}$ carbides of group V transition metals and to a shift of the Fermi level toward the minimum of the curve $N(E)$, where $d\chi/dT > 0$.

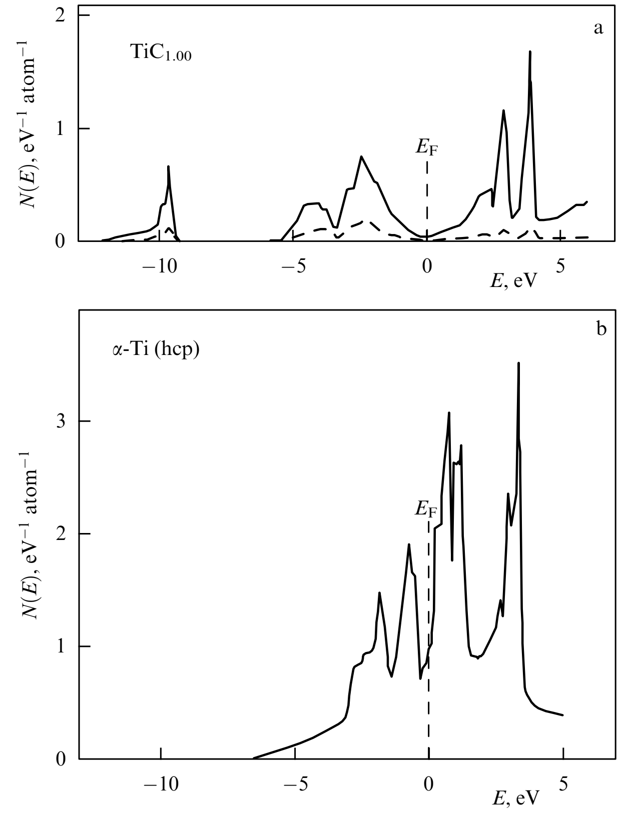

Figure 4. Curves of the density of electronic states $N(E)$ for (a) stoichiometric titanium carbide $TiC_{1.0}$ (the solid curve represents the total density of electronic states, while the dashed curve represents the partial density of states, caused by the electrons of the carbon atoms) [64], and (b) metallic hcp α-Ti [33].

If the cubic carbides, nitrides, and oxides of group IV and V transition metals possessed no wide homogeneity regions, the discussion of their magnetic susceptibility could stop right here. However, the presence of homogeneity regions, within which the concentration of structural vacancies in nonstoichiometric MX_y compounds may be very high (up to 30 – 50 at.%), leads to a situation in which susceptibility depends both on the content of nonmetal X atoms and on the distribution of such atoms in the lattice.

In view of this, we might say that the goal of the present review is not only to generalize the body of information about the magnetic susceptibility of nonstoichiometric compounds in states with different degrees of short- and long-range order (this information can be found in original works) but primarily to focus the attention of researchers on the possibilities of magnetic susceptibility as a rather sensible instrument for studying the fine details in the structure of nonstoichiometric compounds and, in a broader perspective, of various solid-phase systems with atomic substitution. Bearing all this in mind, we focus on three problems in this review: the causes for nonstoichiometric influences on the susceptibility; the experimental study of effects in the behavior of susceptibility that are caused by the redistribution of nonmetal atoms and vacancies in the crystal lattice, and the possibility of using the results of susceptibility measurements in estimating the parameters of short- and long-range order in nonstoichiometric compounds of group IV and V transition d-metals.

2. Magnetic susceptibility of strongly nonstoichiometric compounds

In this section, we briefly discuss the results of research into the magnetic susceptibility of nonstoichiometric carbides, nitrides, and oxides, carried out without taking into account the structural state of these compounds.

Up to 1980, there were no thorough investigations into the magnetic susceptibility of strongly nonstoichiometric compounds MX_y ($X = \mathrm{C}$, N, and O) with a basis cubic structure $B1$. Most measurements of the magnetic susceptibility of nonstoichiometric compounds with different interstitial atom content were carried out in a period from 1960 to 1975, and often the results of different researchers did not agree. Variations in the magnetic susceptibility χ over the homogeneity regions of cubic $M\mathrm{C}_y$ carbides of titanium, zirconium, hafnium, vanadium, niobium, and tantalum, which were detected by several researches (see Refs [46, 56, 58, 59, 65–70], are shown in Fig. 5. Within experimental error, the susceptibility χ of carbides of group IV transition metals almost monotonically decreases with increasing carbon content.

Bittner and Goretzki [65] studied the magnetic susceptibility of several samples of titanium carbide TiC_y with different carbon content at room temperature. They found that TiC_y constitutes a weak paramagnet and its susceptibility χ increases with deviation from the stoichiometric composition (see Fig. 5). A similar dependence of the magnetic susceptibility on the composition of the TiC_y carbide at 300 K was detected by Dubrovskaya et al. [71]. Lesnaya et al. [66] investigated the temperature dependence of the magnetic susceptibility of the titanium carbides $\mathrm{TiC}_{0.72}$, $\mathrm{TiC}_{0.79}$, $\mathrm{TiC}_{0.90}$, and $\mathrm{TiC}_{0.96}$ in the temperature interval from 100 to 1100 K. The paper contains no information

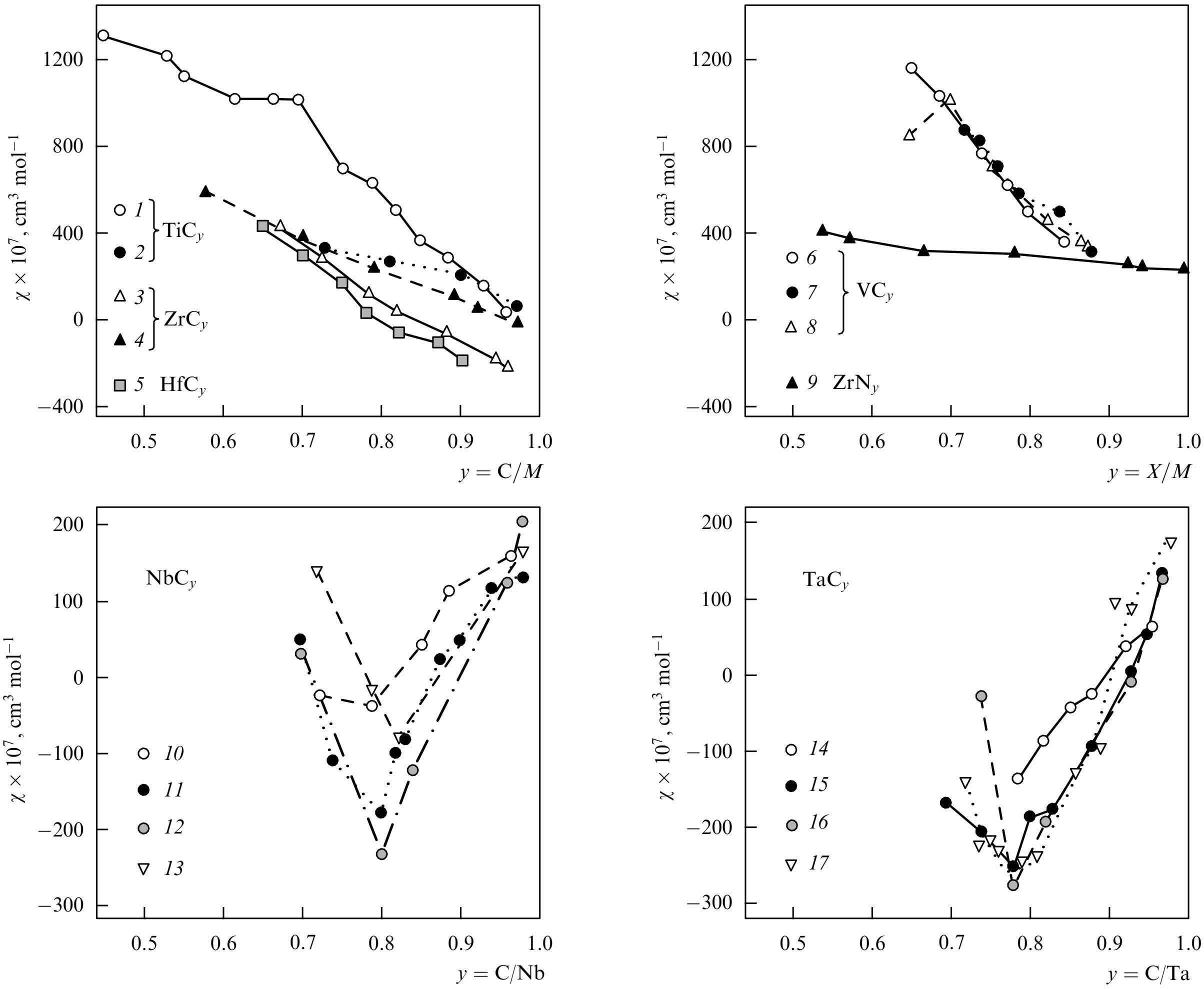

Figure 5. Isotherms of the magnetic susceptibility $\chi(y, T)$ in homogeneity regions of the cubic carbides $M\mathrm{C}_y$ and zirconium nitride ZrN_y. For TiC_y: *1*, $\chi(y, 300)$ [65] and *2*, $\chi(y, 300)$ [66]; for ZrC_y: *3*, $\chi(y, 300)$ [65] and *4*, $\chi(y, 300)$ [56]; for HfC_y: *5*, $\chi(y, 300)$ [65]; for VC_y: *6*, $\chi(y, 300)$ [65]; *7*, $\chi(y, 300)$ [58], and *8*, $\chi(y, 300)$ [46]; for ZrN_y: *9*, $\chi(y, 300)$ [65]; for NbC_y: *10*, $\chi(y, 300)$ [65]; *11*, $\chi(y, 300)$ [67]; *12*, $\chi(y, 100)$ [59], and *13*, $\chi(y, 300)$ [68], and, finally, for TaC_y: *14*, $\chi(y, 300)$ [65]; *15*, $\chi(y, 300)$ [69]; *16*, $\chi(y, 100)$ [69], and *17*, $\chi(y, 300)$ [70].

about the structural state of the samples, but the employed method of synthesizing (hot pressing followed by rapid cooling) suggests that the samples were disordered. No special features were detected in the temperature dependences of the magnetic susceptibility. It must be noted that the researchers did their measurements with very large temperature increments, from 70 to 100 K, so that one cannot expect that any fine effects of the ordering type will be detected. A slightly overestimated absolute value of the magnetic susceptibility suggests that the samples contain a ferromagnetic impurity which Lesnaya et al. [66] were unable to detect, since they did their measurements with a single value of the magnetic field strength.

There are very distinct minima in the concentration dependences $\chi(y)$ of the susceptibility of the carbides TaC_y and NbC_y (see Fig. 5). Borukhovich et al. [59], Bittner and Goretzki [65], and Dubrovskaya and Matveenko [69] studied the behavior of the magnetic susceptibility χ of disordered tantalum carbide within its homogeneity region. According to their data, as the concentration of structural vacancies increases (with decreasing y), the susceptibility of TaC_y decreases, moves from the paramagnetic region to the diamagnetic, reaches its minimum corresponding to the $TaC_{0.78}$ carbide, and then grows as the lower boundary of the homogeneity region is approached. The study of the temperature dependence of susceptibility $\chi(T)$ of tantalum carbide revealed a nonlinear variation of χ with temperature, and the variation was found to strongly depend on the carbide composition [59, 69]. The method of measuring χ used by Dubrovskaya and Matveenko [69] (pre-annealing of the samples at 1200 – 1300 K), could have assisted the transition of TaC_y from a disordered state to an ordered one, whereby several features of $\chi(T)$ dependences established by these researchers could be related to the ordering and disordering that took place during measurements. Some of the features observed by Dubrovskaya et al. [71] in $\chi(T)$ curves of niobium carbide NbC_y could also be related to the ordering that took place during susceptibility measurements. The curve $\chi(y)$ for vanadium carbide VC_y exhibits no minimum of susceptibility, since the homogeneity region of this carbide is limited by the $VC_{0.88}$ composition.

The magnetic susceptibility of the MN_y nitrides has been studied to a much lesser degree than that of carbides. According to Bittner and Goretzki [65] and Goretzki [72], the magnetic susceptibility of zirconium nitride ZrN_y at 300 K linearly decreases with the increase in nitrogen content (see Fig. 5). The values of the susceptibilities χ of stoichiometric or near-stoichiometric nitrides of titanium, vanadium, niobium, and tantalum at 300 K can be found in Refs [44, 72].

The insights into the magnetic properties of strongly nonstoichiometric cubic monoxides TiO_y and VO_y are scarce, although these compounds are unique in their structure. These are the only known compounds containing structural vacancies in both (metallic and oxygen) sublattices, with the vacancy concentration in each sublattice being as high as 20 – 25 at.%. Even the monoxides $TiO_{1.0}$ and $VO_{1.0}$ of equiatomic composition are actually nonstoichiometric compounds: the titanium monoxide $TiO_{1.0}$ contains 16.7 at.% of vacancies in each sublattice [73, 74], while the vanadium monoxide $VO_{1.0}$ contains 15 – 18 at.% of vacancies in each sublattice [75 – 77]. The real composition of titanium and vanadium monoxides TiO_y and VO_y, with allowance for defects in their metallic and oxygen sublattices, should be represented as Ti_xO_z and V_xO_z, where $z/x = y$.

The first to study the variations of the magnetic susceptibility in the homogeneity region of cubic titanium monoxide TiO_y was Ehrlich [78]. Later, Denker [79] and Vasil'ev et al. [80] studied the nonstoichiometry effect on the magnetic susceptibility of TiO_y. According to indirect data, the susceptibility measurements done by Ehrlich [78], Denker [79], and Vasil'ev et al. [80] involved samples of disordered titanium monoxide. Denker [79] measured in the temperature interval from 77 to 300 K the magnetic susceptibility of TiO_y samples ($y = 0.80$, 0.91, 1.00, 1.15, and 1.25) synthesized by zone melting. According to his findings, the studied titanium monoxide constitutes a weak paramagnet with a magnetic susceptibility that only slightly depends on temperature. Vasil'ev et al. [80] measured in the 79 – 373-K temperature range the magnetic susceptibility of eight TiO_y samples ($0.85 \leqslant y \leqslant 1.19$). The data obtained suggest that titanium monoxide is a compound whose paramagnetism is practically temperature-independent. Takeuchi and Suzuki [81] arrived at similar conclusions. They measured the magnetic susceptibility of TiO_y ($0.82 \leqslant y \leqslant 1.23$) in a temperature range from 80 to 500 K. The magnetic susceptibility of TiO_y samples ($y = 0.83$, 1.04, 1.13, 1.23, and 1.30) was also measured by Aivazov et al. [82] at temperatures ranging from 100 to 1000 K; nothing was reported about the structural state of the samples. In the latest studies in this field [83, 84], the magnetic properties of disordered cubic titanium monoxide were measured for the entire homogeneity region at temperatures ranging between 4.2 and 400 K. The concentration dependences of the magnetic susceptibility of titanium monoxide TiO_y, reported in Refs [78 – 81, 83, 84], are in good agreement with each other (Fig. 6), while the value of susceptibility measured by Aivazov et al. [82] is heavily overestimated. Apparently, the TiO_y samples studied by this group of researchers contained a ferromagnetic impurity.

Takeuchi and Suzuki [75] measured the magnetic susceptibility of cubic vanadium monoxides $VO_{0.81}$, $VO_{0.92}$, $VO_{1.02}$, $VO_{1.15}$, and $VO_{1.20}$ in the temperature range from 85 to 500 K. They represented the measured susceptibility as the sum of a temperature-independent contribution and a temperature-dependent contribution obeying Curie's law, i.e., $\chi(T) = \chi_0 + C/T$, where C is the Curie constant. The study by Banus et al. [76] of the VO_y ($0.79 \leqslant y \leqslant 1.32$) magnetic properties at temperatures ranging from 4.2 to 273 K revealed that the temperature dependence of the susceptibility is described by the Curie – Weiss law with an additional, temperature-independent, term, namely, $\chi(T) = \chi_0 + C/(T + \theta)$. As oxygen content in VO_y increases, the temperature-independent term χ_0 and the Curie constant increase exponentially, while the Weiss constant θ first linearly decreases from 8 K, reaching its minimum value of roughly 2 K at $y \approx 1$, and then linearly increases to roughly 9 K. The nonstoichiometry effect on the magnetic susceptibility of vanadium monoxide VO_y ($0.79 \leqslant y \leqslant 1.29$) in the temperature range between 100 and 1000 K was also studied by Aivazov et al. [77], who provided no evidence on the structural state of this substance. Within the investigated temperature and composition intervals, vanadium monoxide VO_y behaves as a paramagnet, and its susceptibility χ at any temperature increases with oxygen content. The dependences of magnetic susceptibility χ on the VO_y composition according to the data of Refs [75 – 77], which are in fairly good agreement with each other, are shown in Fig. 6. The special feature of vanadium monoxide that sets it apart from other cubic nonstoichiometric compounds is its very strong para-

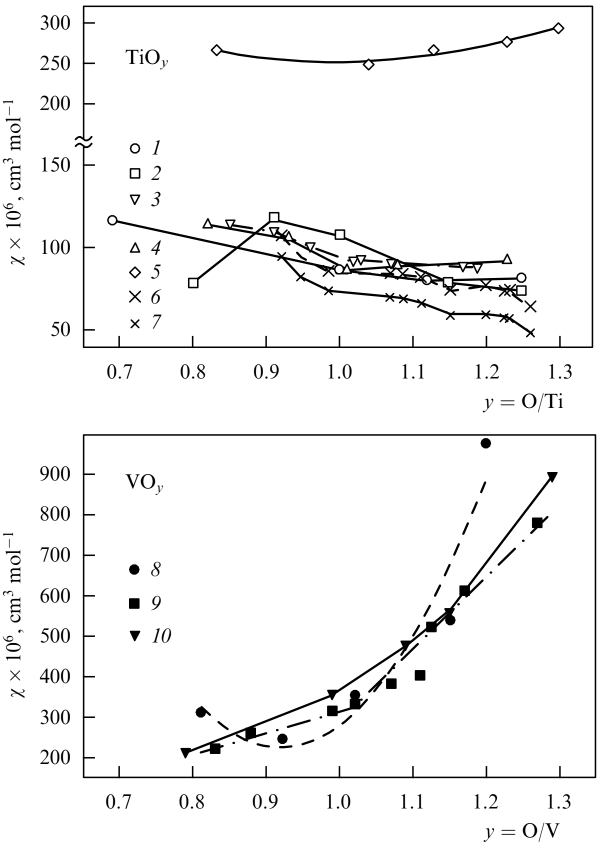

Figure 6. Variations in the magnetic susceptibility $\chi(y)$ in the homogeneity regions of the cubic monoxides TiO$_y$ and VO$_y$ at 300 K: *1*, [78]; *2*, [79]; *3*, [80]; *4*, [81]; *5*, [82]; *6*, [83, 84]; *7*, [83, 84]; *8*, [75]; *9*, at $T = 273$ K [76], and *10*, [77]. Curves *1–6* and *8–10* representing the molar magnetic susceptibility of TiO$_y$ and VO$_y$ are given per mole of TiO$_y$ and VO$_y$, i.e., without allowing for defects in the metal sublattice, while curve *7* was constructed with allowance for the defects in the titanium sublattice, i.e., per mole of Ti$_x$O$_z$, as susceptibility given in Refs [83, 84].

magnetism. According to Mott [85], the cause for the strong paramagnetism of VO$_y$ is the substantial electron–electron coupling, in view of which the current carriers in VO$_y$ constitute a highly correlated electron gas; moreover, the formation of polarons leads to a substantial increase in the effective electron mass.

Note that the molar magnetic susceptibility of titanium and vanadium monoxides in Refs [75–82] was obtained without allowance for defects in the metallic sublattices of these compounds, i.e., on a per-mole basis for TiO$_y$ and VO$_y$ rather than per mole of Ti$_x$O$_z$ and V$_x$O$_z$. In Refs [83, 84], the molar susceptibility of TiO$_y$ was given with allowance for defects in the titanium sublattice, i.e., per mole of Ti$_x$O$_z$. For the sake of the convenience in comparing the results of different researchers, the dependence $\chi(y, 300)$ in Fig. 6 [83, 84] is given per mole of Ti$_x$O$_z$, and per mole of TiO$_y$.

Thus, the earlier inquiries into the magnetic susceptibility of nonstoichiometric compounds established the very fact that there is a variation of susceptibility with the composition of these compounds, although the results of different researchers do not always agree with each other and cannot always be reproduced. One of the main reasons for such a discrepancy is the absence of any real means for accounting for the structural state of the substances being studied. In view of this, we examine in Section 3 the experimental results obtained for nonstoichiometric compounds whose structural state (disordered or ordered) was determined through special studies of their crystal structures.

3. Ordering effects on the magnetic susceptibility of nonstoichiometric compounds

The experimental results concerning the magnetic susceptibility of strongly nonstoichiometric MX_y compounds are usually analyzed without any regard for the possible ordering of interstitial atoms and structural vacancies, namely, without examining the possible redistribution of nonmetal atoms and vacancies over the sites of the basis crystal structure $B1$. As a result, the real structural state (the degree of order) of the compound is not taken into account. The magnetic susceptibility χ is one of the few properties of a solid that is determined solely by the electron subsystem and does not depend directly on the phonon energy spectrum. However, the change in the mutual arrangement of the atoms in the crystal lattice, caused by ordering, may inflict changes on the electron structure, changes that will manifest themselves in the behavior of the magnetic susceptibility (among other things). Thanks to this, research into the susceptibility of ordered and disordered phases of strongly nonstoichiometric compounds provides an understanding of the interrelation between the electronic structure and the formation of this or that superstructure.

The ordering effect on the magnetic susceptibility of a nonstoichiometric compound was first detected and explained in Refs [60, 86–88]. The compound in question was niobium carbide NbC$_y$. Later studies dealt with changes in susceptibility χ in the course of phase disorder–order transformations in the nonstoichiometric titanium carbides TiC$_y$ [55, 89], hafnium carbides HfC$_y$ [57, 90–92], and tantalum carbides TaC$_y$ [61, 93, 94]. Various researchers (see Refs [55, 57, 61, 89–94]) explained the observed differences in the susceptibilities of disordered and ordered carbides TiC$_y$, HfC$_y$, NbC$_y$, and TaC$_y$ using a model developed for studies of the magnetic susceptibility of niobium carbide NbC$_y$. For this reason, we will discuss the results presented in Refs [60, 86–88] in greater detail.

The magnetic susceptibility χ of niobium carbide NbC$_y$ within the homogeneity region of the cubic phase (from NbC$_{0.70}$ to NbC$_{1.00}$) was studied by Borukhovich et al. [59], Bittner and Goretzki [65], Matveenko et al. [67], and Genkin et al. [68]. According to the results of their research, the susceptibility of NbC$_y$ rapidly decreases with carbon content, passing from the paramagnetic region to the diamagnetic region, reaches its minimum near the composition NbC$_{0.79}$ [65], NbC$_{0.80}$ [59, 67], or NbC$_{0.82}$ [68], and then again rises to paramagnetic values (see Fig. 5). Studies of the susceptibility of cubic niobium carbide NbC$_y$ done by Borukhovich et al. [59] and Matveenko et al. [67] within a wide temperature range showed that the dependences $\chi(T)$ are nonlinear functions of temperature and change significantly with the composition of NbC$_y$. Note that these investigations involved NbC$_y$ samples synthesized under various conditions without allowance for the possible ordering of carbon atoms. However, today we know that nonstoichiometric niobium carbide in the temperature range between 1260 and 1355 K and in the range of compositions from NbC$_{0.81}$ to NbC$_{0.88}$ undergoes an equilibrium, reversible disorder–order transformation [86, 95–98] and there forms an ordered phase Nb$_6$C$_5$ which possesses a homogeneity region. It can be

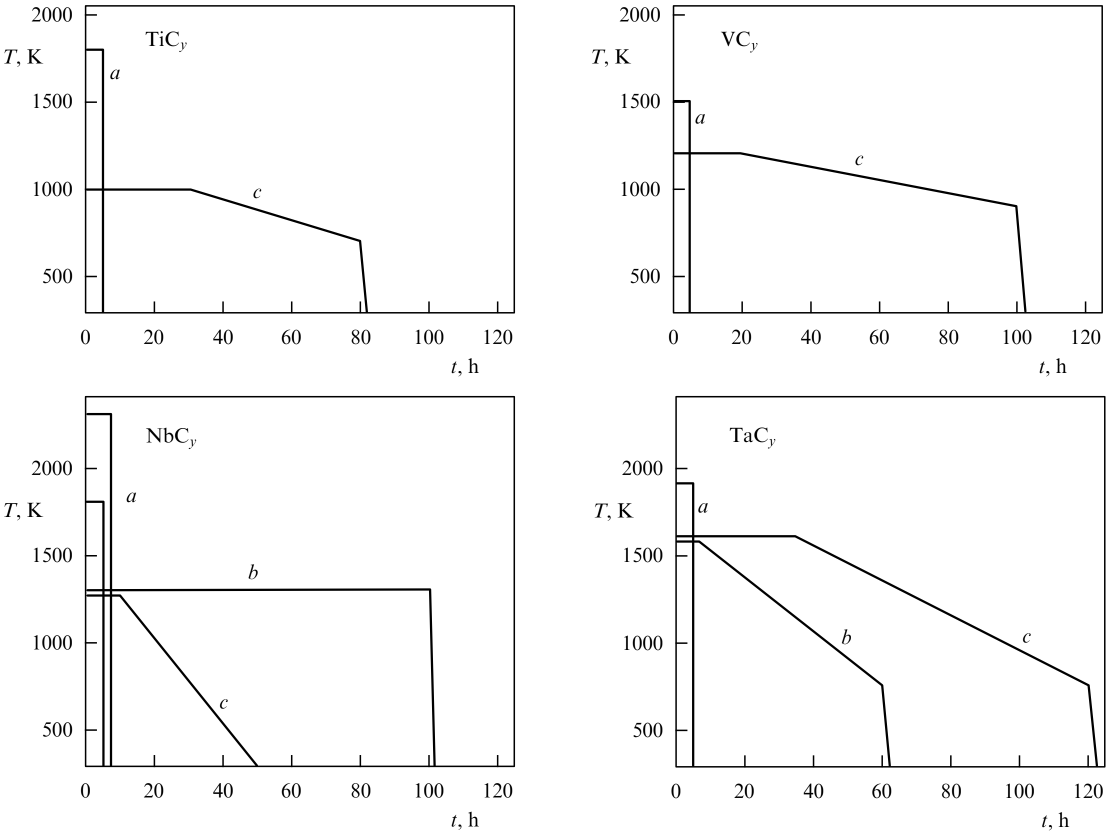

Figure 7. Thermal treatment modes used by various researchers (see Refs [55, 57, 60, 61, 86–94, 99, 100]) to synthesize titanium carbide TiC$_y$, vanadium carbide VC$_y$, niobium carbide NbC$_y$, and tantalum carbide TaC$_y$ in disordered and ordered states: *a*, quenching to synthesize disordered carbides; *b* and *c*, annealing to synthesize nonstoichiometric carbides in states with different degrees of long-range order.

assumed that certain features of the dependence $\chi(T)$ for niobium carbide [67] are related to ordering that happens during susceptibility measurements.

A team of researchers (see Refs [60, 86–88]) measured the magnetic susceptibility χ in a wide temperature interval from 300 to 1300 K and used in their measurements samples of niobium carbide that were both in ordered and disordered states. The structural state of the samples was monitored by the neutron diffraction method. The NbC$_y$ samples with different degrees of order were produced using three thermal treatment modes (see Fig. 7). The disordered samples were prepared by quenching (mode *a*); as a result of thermal treatment by mode *b*, the samples contained disordered and ordered phases simultaneously; finally, thermal treatment by mode *c* ensured the synthesis of an ordered carbide. The magnetic susceptibility was measured by maintaining the measurement temperature for a time that guaranteed a constant, time-independent, value of χ.

A typical temperature dependence of the susceptibility $\chi(T)$ of niobium carbide experiencing ordering is shown in Fig. 8. Measurements of the susceptibility of the disordered carbide NbC$_{0.83}$ quenched from a temperature amounting to roughly 2000 K, which is much higher than T_{trans}, revealed a sudden drop in χ to values characteristic of ordered carbide with the same composition. The neutron diffraction patterns of NbC$_y$ ($0.81 \leqslant y \leqslant 0.88$) samples taken after measuring the temperature dependence of susceptibility showed up the presence of superstructure reflections. This suggests that ordering takes place during measurement. It is worth noting that the observed temperature $T_{\text{trans}}^{\text{noneq}}$ of the irreversible

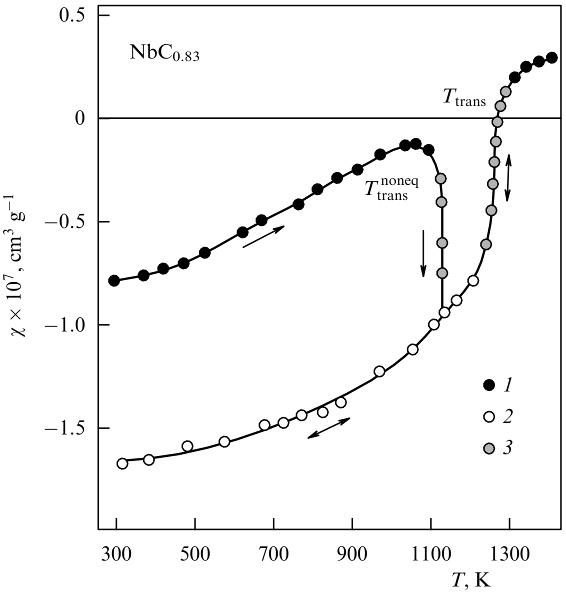

Figure 8. Ordering effect on the magnetic susceptibility χ of the niobium carbide NbC$_{0.83}$ [60, 87]: *1*, disordered state; *2*, ordered state, and *3*, transient state. The rapid irreversible drop in χ at $T_{\text{trans}}^{\text{noneq}} = 1120$ K is the consequence of an irreversible transition from the quenched none-quilibrium disordered state into an equilibrium ordered state. The jump-like reversible variation of χ at $T_{\text{trans}} \approx 1300$ K corresponds to an equilibrium reversible order–disorder transformation. The arrows indicate the directions in which the temperature changes.

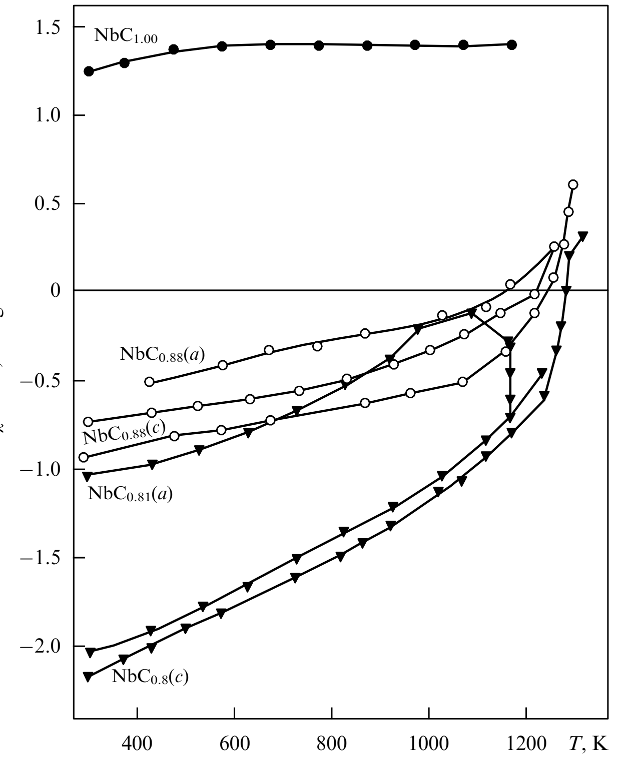

Figure 9. Ordering effect on the magnetic susceptibility χ of niobium carbides NbC_y [60, 87]; *a* and *c* correspond to the thermal treatment modes according to Fig. 7.

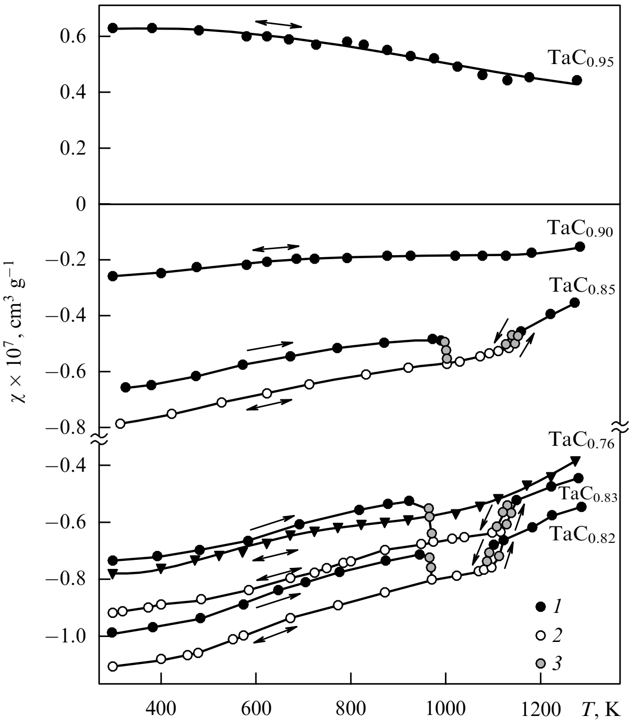

Figure 11. Ordering effect on the magnetic susceptibility χ of tantalum carbides TaC_y [61, 93, 94]: *1*, disordered state; *2*, ordered state, and *3*, transient state. The arrows indicate the directions in which the temperature changes.

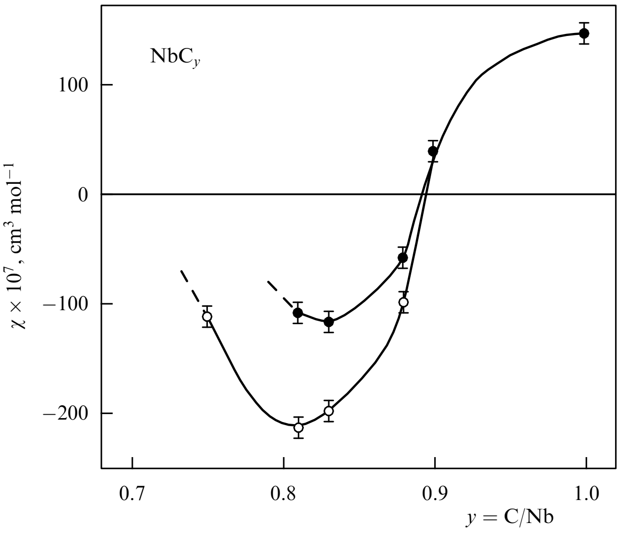

Figure 10. Magnetic susceptibility χ as a function of the composition of disordered (●) and ordered (○) niobium carbides NbC_y at $T = 300$ K [60].

transition from a quenched, nonequilibrium, disordered state into an equilibrium, ordered state must be distinguished from the temperature T_{trans} of the reversible equilibrium order–disorder transition (see Fig. 8).

The curves representing the temperature dependence of the susceptibility of NbC_y samples with carbon content y ranging from 0.81 to 0.88 have the same shape (Fig. 9) as $\chi(T)$ for the $NbC_{0.83}$ carbide.

Measurements of the magnetic susceptibility at $T = 300$ K showed that the minima in the $\chi(y)$ curves for the NbC_y carbides in the disordered and ordered states correspond to the $NbC_{0.83}$ and $NbC_{0.81}$ carbides (Fig. 10). This explains the difference in the experimental data [59, 67, 68] by the fact that in these studies the niobium carbide samples used in susceptibility measurements were in states with different degrees of order.

Ordering effect on the magnetic susceptibility of the tantalum carbide TaC_y was studied by Lipatnikov et al. [61, 93, 94]. The researchers found that the slow heating of the samples of quenched tantalum carbides $TaC_{0.82}$, $TaC_{0.83}$, and $TaC_{0.85}$ was accompanied by an irreversible lowering of the susceptibility χ at temperatures in the 960–1000-K range, which had never been observed before (Fig. 11). The temperature at which the jump-like drop in χ occurs is, apparently, the temperature of the beginning of diffusion of carbon atoms in TaC_y and corresponds to an irreversible transition from a quenched, nonequilibrium, disordered state to an equilibrium ordered state. Indeed, annealing taking place in the course of susceptibility measurements up to $T < 1000$ K leads to the appearance of a set of superstructure reflections on the neutron diffraction patterns of $TaC_{0.82}$, $TaC_{0.83}$, and $TaC_{0.85}$, which suggests the formation of an ordered phase.

With a further rise in temperature, susceptibility smoothly increases, but then increases very suddenly at T_{trans} equal to 1090, 1130, and 1150 K for $TaC_{0.82}$, $TaC_{0.83}$, and $TaC_{0.85}$ samples, respectively. Magnetic susceptibility measurements involving these samples showed the presence of susceptibility hysteresis (as the temperature is lowered) in temperature intervals from 1070 to 1090 K, from 1100 to 1130 K, and from 1120 to 1150 K for $TaC_{0.82}$, $TaC_{0.83}$, and $TaC_{0.85}$ (see Fig. 11). The reversible jump in susceptibility corresponding to the region of temperature hysteresis in the $\chi(T)$ curves is

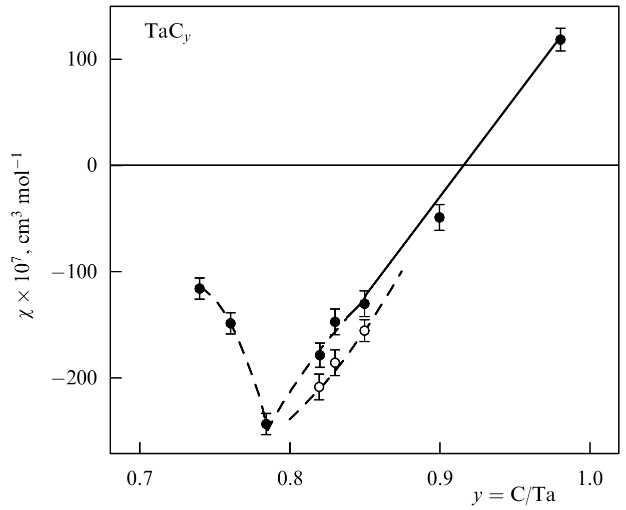

Figure 12. Magnetic susceptibility χ as a function of the composition of disordered (●) and ordered (○) tantalum carbides TaC$_y$ at $T = 300$ K [94].

caused by an equilibrium order–disorder structural transformation. The presence of hysteresis along with two-phase region testifies that this transformation constitutes a first-order phase transition. A further decrease in temperature leads to a lowering of the susceptibility of the TaC$_y$ samples, and within the entire temperature range $T < T_{\text{trans}}^{\text{noneq}}$ the value of χ for the annealed (in the process of measuring susceptibility) carbide TaC$_y$ ($0.82 \leqslant y \leqslant 0.85$) is smaller than the value for a quenched sample of the same composition (see Fig. 11). The temperature dependences of the susceptibility of the tantalum carbide samples annealed by mode *c* (see Fig. 7) and annealed in the course of measuring the susceptibility χ coincide. No special features were observed in the temperature curves $\chi(T)$ for TaC$_y$ carbides with $y < 0.80$ and $y > 0.90$, since these tantalum carbide compositions 'lie' outside the TaC$_{0.79}$–TaC$_{0.89}$ region in which, according to neutron diffraction measurements, an incommensurate ordered phase close to the M_6C_5 type is formed [101].

The measurements demonstrated that ordering is accompanied by a reduction in the magnetic susceptibility of tantalum carbide (Fig. 12); the largest difference in the susceptibilities of TaC$_y$ carbides in the disordered and ordered states, $\Delta\chi = \chi_{\text{disord}} - \chi_{\text{ord}}$, is observed in the carbide TaC$_{0.83}$.

Another nonstoichiometric compound whose ordering was studied by measuring its magnetic susceptibility is titanium carbide TiC$_y$. Among all cubic carbides, TiC$_y$ has the widest homogeneity region $0.48 \leqslant y \leqslant 1.00$ [1, 2] and, according to the experimental structural data [102–107] and the calculated results [3, 4, 107–109], ordered Ti$_2$C, Ti$_3$C$_2$, and Ti$_6$C$_5$ phases form in it.

According to Bittner and Goretzki [65], the carbide TiC$_{0.96}$ constitutes a paramagnet with a susceptibility close to zero; as the deviation from stoichiometry gets larger, the susceptibility χ of titanium carbide increases, and within the TiC$_{0.62}$–TiC$_{0.70}$ range this quantity is almost constant (see Fig. 5).

Zueva et al. [55, 89] studied the temperature dependence of the susceptibility, $\chi(T)$, of titanium carbide with different carbon content and found that susceptibility increases nonlinearly with a rise in temperature (Fig. 13). The magnetic susceptibility of the carbides TiC$_{0.83}$, TiC$_{0.90}$, TiC$_{0.925}$, TiC$_{0.94}$, and TiC$_{1.00}$ was found to increase without any effects that would indicate the presence of phase transformations. The temperature curves of susceptibility, $\chi(T)$, for the carbides TiC$_{0.50}$, TiC$_{0.55}$, TiC$_{0.59}$, TiC$_{0.63}$, TiC$_{0.68}$, TiC$_{0.69}$, and TiC$_{0.81}$ exhibited an anomalous drop in χ in the 750–950-K range, while a further increase in temperature again pushed χ up (see Fig. 13). Diffraction studies showed that these variations of the magnetic susceptibility were related to ordering and subsequent disordering of titanium carbide — that is, to processes taking place on heating. The presence of a small hysteresis loop in the transformation region (see Fig. 13) implies that ordering in titanium carbide is a phase transition close to a first-order one.

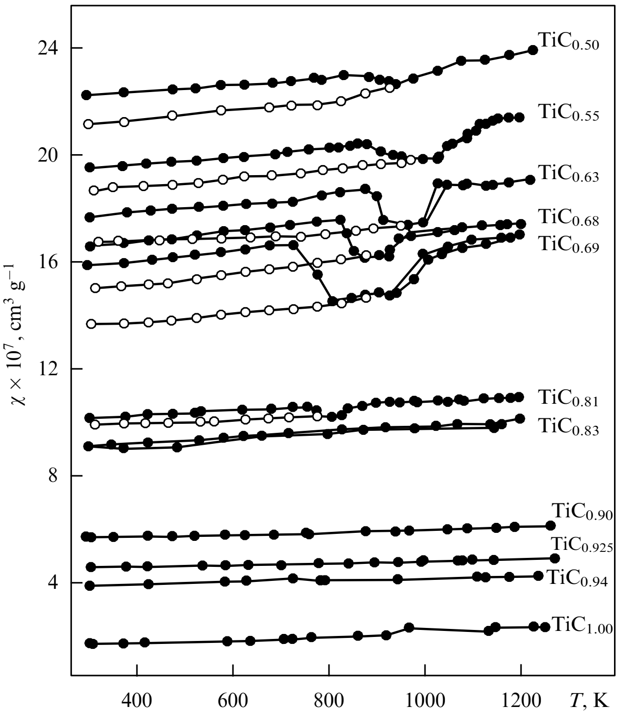

Figure 13. Temperature dependences of the magnetic susceptibility χ of nonstoichiometric titanium carbides TiC$_y$ in disordered (●) and ordered (○) states [55, 89].

The ordering of titanium carbide TiC$_y$ is accompanied by a decrease in the magnetic susceptibility by $(40-120) \times 10^{-7}$ cm^3 mol^{-1}, depending on the carbide's composition (Fig. 14). A similar effect is observed when niobium and tantalum carbides experience ordering: for NbC$_{0.83}$ and TaC$_{0.83}$ at 300 K, the value of $\Delta\chi = \chi_{\text{disord}} - \chi_{\text{ord}}$ equals 76×10^{-7} and 39×10^{-7} cm^3 mol^{-1}, respectively.

An attempt to study the ordering effect on the magnetic susceptibility of nonstoichiometric titanium carbide was also made by Dubrovskaya et al. [71], who measured the susceptibility in the 300–1300-K range. The researchers utilized the TiC$_{0.59}$ carbide quenched from 1270 K (the cooling rate is unknown) and the carbides TiC$_{0.59}$, TiC$_{0.65}$, and TiC$_{0.74}$ annealed from 1270 to 970 K with a rate of 50 K h^{-1} and then cooled to 300 K in the course of three hours. It was assumed that in the annealed samples there was an ordered phase Ti$_8$C$_5$ (modern structural data do not corroborate this assumption). The magnetic susceptibility of the TiC$_y$ samples in question was found to increase slightly with temperature. The only observed peculiarities were

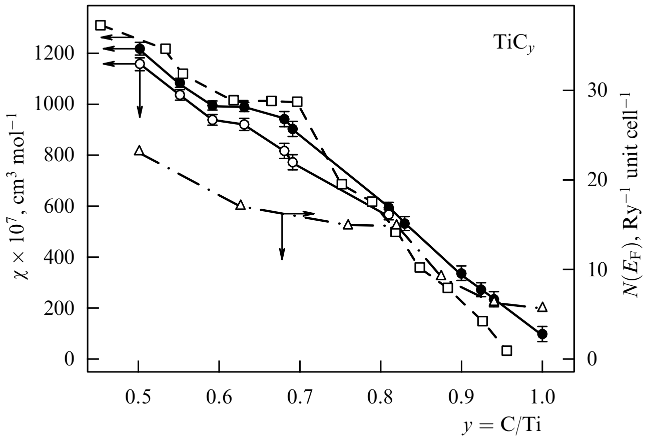

Figure 14. Variations of the magnetic susceptibility χ at 300 K and density of electronic states at the Fermi level, $N(E_F)$, within the homogeneity region of cubic titanium carbides TiC$_y$: susceptibilities of disordered (●) and ordered (○) titanium carbide TiC$_y$ according to the data from Refs [55, 89]; □, data from Ref. [65] on the susceptibility of disordered titanium carbide, and △, the density of states $N(E_F)$ at the Fermi level [38].

displayed by a bend in the $\chi(T)$ curve for the quenched carbide TiC$_{0.59}$ and the increase in the temperature coefficient $d\chi/dT$ at about 1000 K. It was also found that the temperature dependence $\chi(T)$ for the annealed carbide TiC$_{0.59}$ is linear. The magnetic susceptibility of the quenched carbide TiC$_{0.59}$ in the temperature range from 800 to 1000 K, where ordering takes place [55, 103], was measured with a 100-K increment, with the result that Dubrovskaya et al. [71] were unable to distinctly detect an ordering effect. The absence of ordering effects in the $\chi(T)$ dependence for the TiC$_{0.74}$ carbide is due to the fact that in its composition the carbide TiC$_{0.74}$ 'lies' outside the homogeneity region of the ordered phases. Indeed, the main ordered phase of titanium carbide is Ti$_2$C which exists at temperatures below 1000 K within the TiC$_{0.48}$ – TiC$_{0.58-0.59}$ range; on the interval TiC$_{0.63}$ – TiC$_{0.67}$ there may emerge the ordered phase Ti$_3$C$_2$ [105]. Variations in susceptibility can, apparently, be observed in a TiC$_{0.65}$ carbide in the process of transforming from a quenched disordered state to an equilibrium ordered state, but Dubrovskaya et al. [71] did not measure the susceptibility of the disordered carbide TiC$_{0.65}$. Thus, as a result of employing an erroneous method, the researchers were unable to establish how ordering affects the magnetic susceptibility of nonstoichiometric titanium carbide.

The least thoroughly studied compound belonging to the group of strongly nonstoichiometric refractory compounds is hafnium carbide HfC$_y$. This carbide has never been systematically studied, and either nothing is known about its electronic and crystal structures or the dependence of its physical properties on composition and temperature, or the data are scant and are 40 to 50 years old.

For a long time, the literature contained no experimental data on the ordering of nonstoichiometric hafnium carbide HfC$_y$. The reason is that it is practically impossible to directly study the structure of the ordered HfC$_y$ phases by diffraction methods: in an X-ray diffraction experiment, the relative intensity of the possible superstructure reflections is very low because of the large difference in the amplitudes of X-ray scattering by Hf and C atoms, while in the case of diffraction of neutrons the absorption of the latter by the massive hafnium nuclei is very large, so that the total intensity of the diffraction spectrum is low and it is practically impossible to observe superstructure reflections. NMR cannot be applied to studying the atomic distribution in the crystal lattice of HfC$_y$ because the most abundant isotopes of hafnium, ^{180}Hf, ^{176}Hf, and ^{174}Hf, and of carbon, ^{12}C, have spin-0 nuclei, so that they do not possess either a magnetic moment or a quadrupole electric moment.

At the same time, the results of theoretical calculations (see Refs [3, 4, 110, 111]) show that the disordered state of the HfC$_y$ carbide is a thermodynamically equilibrium one at temperatures above 800 K, while at lower temperatures the ordered Hf$_3$C$_2$ and Hf$_6$C$_5$ phases of hafnium carbide must occur in thermodynamic equilibrium conditions. The disordered HfC$_y$ carbide quenched from a temperature of about 2000 K can exist for an indefinitely long time at $T < 800$ K as a metastable nonequilibrium phase, since the rate of diffusion processes at temperatures below 800 K is very low and it is very difficult to reach an equilibrium ordered state via annealing. Thus, the theoretically predicted ordering of nonstoichiometric hafnium carbide HfC$_y$ is arduous to detect in experiments.

Since a direct study of the ordering of nonstoichiometric hafnium carbide HfC$_y$ by structural methods is impossible, a team of researchers (see Refs [57, 90 – 92]) employed an indirect method of investigating disorder – order transitions that uses the results of magnetic susceptibility measurements. They based their reasoning on the previous studies of nonstoichiometric niobium and tantalum carbides [60, 61, 86, 87, 93, 94], which showed that the magnetic susceptibility χ is highly sensitive to electron-structure variations accompanying the transitions from disordered states to ordered states and back.

The samples utilized in this method were those of disordered hafnium carbide HfC$_y$ with varying carbon content ($y = 0.62$, 0.71, 0.78, 0.80, 0.83, 0.87, 0.90, and 0.96), obtained by solid-phase vacuum synthesis at 2200 K with subsequent quenching from 2200 to 300 K with a rate of 2000 K min^{-1}. All samples were homogeneous and consisted of one phase with the $B1$ structure. Susceptibility measurements were done by using a highly sensitive magnetic balance intended for experiments with weak para- and diamagnets, with field strengths 7.2, 8.05, and 8.8 kOe in a temperature range between 300 and 1250 K and in a vacuum no worse than 0.001 Pa. The sensitivity of the balance reached 2×10^{-10} cm^3 g^{-1}. The susceptibility of the studied hafnium carbide was found to be independent of the magnetic field strength, which suggests that there were no ferromagnetic impurities in the samples. Measurements were done with an exposure of 1.5 to 2.0 hours for each temperature, long enough for a constant, time-independent, value of χ to set in.

The study of the $\chi(T)$ dependences showed that the susceptibility of the carbides HfC$_{0.62}$, HfC$_{0.80}$, HfC$_{0.87}$, HfC$_{0.90}$, and HfC$_{0.96}$ increases nonlinearly with temperature without any effects that would point to the presence of phase transitions. The curves $\chi(T)$ for the HfC$_{0.71}$, HfC$_{0.78}$, and HfC$_{0.83}$ carbides exhibit an anomalous decrease in χ in the 835 – 860-K range, followed by an increase in χ under a subsequent rise in temperature (Fig. 15). According to calculations (see Refs [4, 110]), the ordered Hf$_3$C$_2$ and Hf$_6$C$_5$ phases form in hafnium carbide, and the transition temperature T_{trans} for these phases varies between 600 and 800 K, depending on the composition of the disordered carbide. One can assume that the observed anomalous drop in the hafnium carbide susceptibility and its ensuing increase are related to

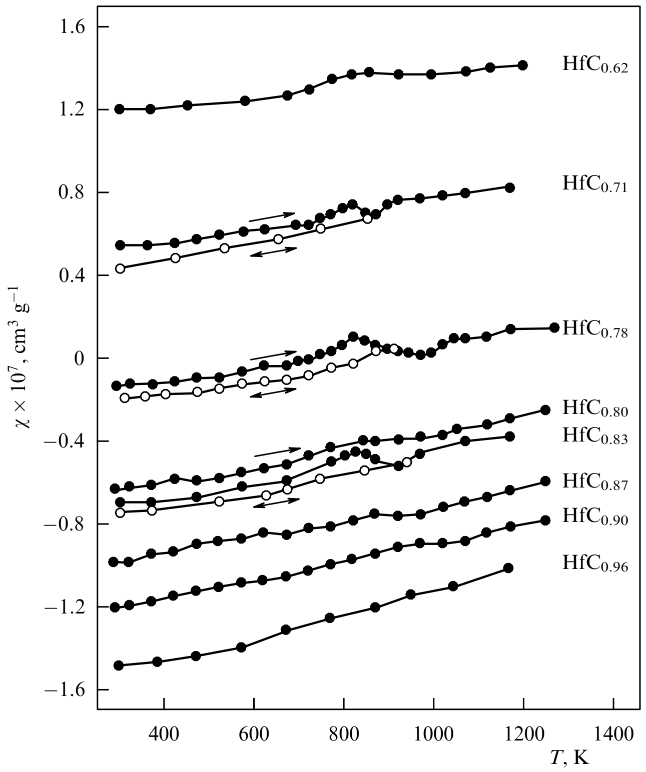

Figure 15. Ordering effect on the magnetic susceptibility χ of hafnium carbides HfC$_y$ [57, 90–92]: disordered (●) and ordered (○) states. The arrows indicate the directions in which the temperature changes.

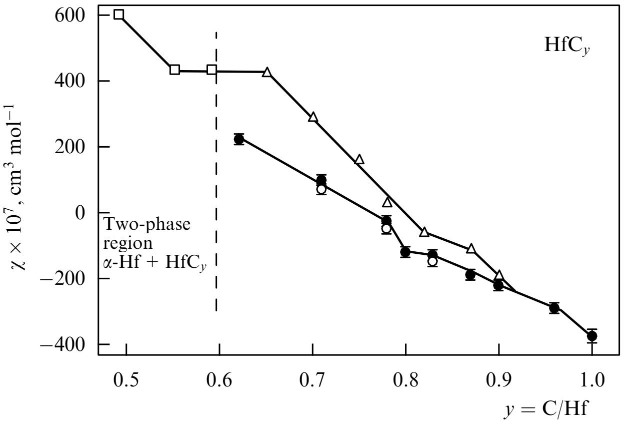

Figure 16. Magnetic susceptibility χ as a function of the composition of hafnium carbides HfC$_y$ at $T = 300$ K: susceptibilities of a single-phase (△) disordered hafnium carbide HfC$_y$ and of two-phase (□) samples (Hf + HfC$_y$) [65]; susceptibilities of disordered (●) and ordered (○) hafnium carbides HfC$_y$ [90]; the vertical dashed line indicates the lower boundary of the HfC$_y$ homogeneity region.

the ordering and subsequent disordering that take place during measurements.

The presence of weak hysteresis in the region of the equilibrium order–disorder transformation implies that ordering in HfC$_y$ comprises a first-order phase transformation. One interesting experimental result is the zero susceptibility of HfC$_{0.78}$, which remains such over the temperature range from 910 to 980 K (see Fig. 15). The absence of salient features in the dependence $\chi(T)$ for the HfC$_{0.80}$ carbide (see Fig. 15) probably means that this carbide 'lies' (in composition) at the boundary separating the regions of existence of the ordered Hf$_3$C$_2$ and Hf$_6$C$_5$ phases and, hence, does not undergo ordering. To form the possible short- and long-range order, the HfC$_{0.80}$ powder was additionally annealed at 750 K over the course of 20 hours and then studied by the TEM method with a JEM-200C microscope [57, 92]. The electron diffraction patterns of individual grains in the HfC$_{0.80}$ carbide revealed the presence of only a system of point reflections from the planes of the reciprocal lattice of the cubic HfC$_y$ phase. Thus, these patterns confirmed the absence of short- and long-range order in the vacancy distribution for HfC$_{0.80}$.

The dependence of the magnetic susceptibility χ on the relative carbon content in HfC$_y$ at $T = 300$ K is shown in Fig. 16. Earlier, Bittner and Goretzki [65] studied the magnetic susceptibility of HfC$_y$ in its homogeneity region at room temperature; hafnium carbide whose composition is close to the stoichiometric is a diamagnet; as the deviation from the stoichiometric composition increases, the magnetic susceptibility rises, and finally the carbide becomes a paramagnet with a composition near that of HfC$_{0.82}$. According to Refs [57, 90, 91], the magnetic susceptibility of HfC$_y$ on the interval $0.6 < y < 0.9$ is somewhat lower than the one measured by Bittner and Goretzki [65]; at $y = 0.9$, the susceptibility data from Ref. [65] and Refs [57, 90] coincide almost perfectly (see Fig. 16). The slight overestimation of the values of the hafnium carbide susceptibility studied by Bittner and Goretzki [65] might be related to the presence of a small amount (~ 0.01 at.%) of ferromagnetic impurity in the carbide.

The ordering in the HfC$_{0.71}$, HfC$_{0.78}$, and HfC$_{0.83}$ carbides leads to a slight decrease in magnetic susceptibility (see Fig. 16). For hafnium carbide, the ordering effect on susceptibility is much smaller in magnitude than for niobium, tantalum, and titanium carbides: at $T = 300$ K, the value of $\Delta\chi = \chi_{\text{disord}} - \chi_{\text{ord}}$ for HfC$_{0.83}$ measures only 9×10^{-7} cm^3 mol^{-1}.

The results of measurements on the magnetic susceptibility χ of nonstoichiometric ordered vanadium carbide V$_8$C$_7$ (VC$_{0.875}$) can be found in Refs [112–114]. The investigated vanadium carbide constituted a nanocrystalline powder, with the nanostructure formed by a disorder–order transition in which the period of the basis cubic crystal lattice with a *B*1 structure increased jump-like from 0.41638 to 0.41685 nm, i.e., by almost 0.0005 nm [114–117]. The susceptibility was measured in 7.2-, 8.05-, and 8.8-kOe magnetic fields on a temperature interval from 300 to 1200 K and found to be independent of the magnetic field strength, which suggested that the carbide contained no ferromagnetic impurities.

The temperature dependence $\chi(T)$ for the nanocrystalline ordered vanadium carbide V$_8$C$_7$ (Fig. 17) within experimental error agrees with Borukhovich and Volkova's data [58] for the coarse-crystalline disordered VC$_{0.88}$ carbide, the only difference being a smaller value of the temperature coefficient dχ/dT. The temperature curve $\chi(T)$ for the susceptibility was found to have no salient features that would indicate the presence of disordering as the temperature increased. This is probably related to the fact that the maximum temperature at which susceptibility was measured ($\sim$ 1200 K) is lower than the order–disorder V$_8$C$_7$–VC$_{0.875}$ transition temperature equal to 1330–1420 K [99, 100, 118–122]. Thus, the ordering effect on the magnetic susceptibility of nonstoichiometric vanadium carbide has yet to be studied. The magnetic susceptibility of nonstoichiometric zirconium

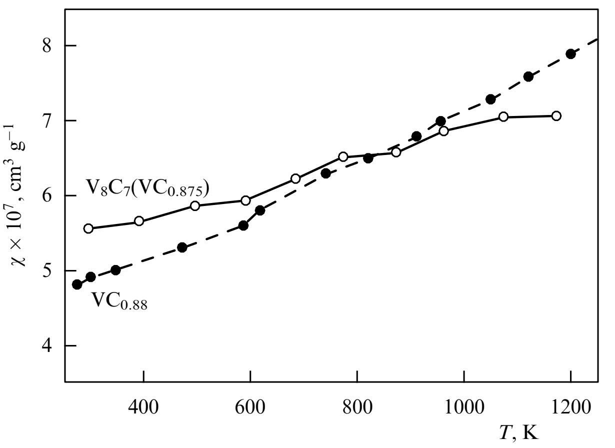

Figure 17. Temperature dependences of the magnetic susceptibility χ of nonstoichiometric vanadium carbide: ●, the disordered $VC_{0.88}$ carbide [58], and ○, the nanocrystalline ordered V_8C_7 ($VC_{0.875}$) carbide [112 – 114].

carbide with allowance for the carbide's structural state has not yet been investigated, either.

On the whole, the results given in Refs [55, 57, 60, 61, 86 – 94] have shown that the magnetic susceptibility of nonstoichiometric compounds is extremely sensitive to structural phase transformations of the disorder – order and order – disorder types and can be used for detecting such transformations. The variations of magnetic susceptibility χ, which were observed in this research, are caused by changes in the composition of nonstoichiometric MC_y carbides, on the one hand, and by ordering effects, on the other. In the sections that follow we examine the possible reasons for such variations.

4. Nonstoichiometry effect on the magnetic susceptibility of carbides and nitrides

As noted earlier, the magnetic susceptibility of nonstoichiometric compounds of transition d-metals is largely similar to the susceptibility of these metals and incorporates the same (true, slightly modified) main contributions. Generally, the magnetic susceptibility χ of conducting substances that possess no spontaneous magnetization, i.e., exhibit no magnetic order, can be written as follows:

$$\chi = \chi_p^- + \chi_{orb} + \chi_{so} , \tag{3}$$

where χ_p^- is the Pauli paramagnetism of the conduction electrons, which makes the main positive contribution to the susceptibility; χ_{orb} is the contribution to susceptibility related to the orbital motion of electrons, and χ_{so} is the contribution provided by spin – orbit coupling. In their relativistic calculations for vanadium, Yasui and Shimizu [123] showed that in magnitude the contribution χ_{so} is much smaller than the other two contributions to susceptibility, with the result that it can be ignored; in the calculations by Bakonyi et al. [33] of Ti, Zr, and Hf susceptibilities, the contribution χ_{so} was also assumed to be small, and so it could also be ignored. The orbital contribution χ_{orb} to the susceptibility can be broken down into the following components:

$$\chi_{orb} = \chi_d^- + \chi_{VV\text{-}orb} + \chi_p^+ + \chi_d^+ , \tag{4}$$

where $\chi_d^- = -(m_0/m^*)^2\chi_p^-(0)/3$ is the Landau diamagnetism of conduction electrons (m_0 is the free electron mass, and m^* is the effective electron mass); $\chi_{VV\text{-}orb}$ is the Van Vleck orbital paramagnetism, and χ_p^+ and χ_d^+ are the para- and diamagnetism of the ion cores (filled electron shells). If we combine expansion (4) with the susceptibility (3) of transition d-metals, we have

$$\chi = \chi_p^- + \chi_d^- + \chi_{VV\text{-}orb} + \chi_p^+ + \chi_d^+ . \tag{5}$$

Note that the first three terms in formula (5) are composite integral functions of both the Fermi distributions, which give the probability of finding the electron in a state with a definite energy $E(\mathbf{k})$, and operators of spin or orbital moments, whose matrix elements link electron states with different wave vectors $\mathbf{k}$. Hence, to calculate the susceptibility, we must at least know the dispersion law $E(\mathbf{k})$ and the electron wave functions.

In accordance with equation (5), the measured magnetic susceptibility of nonstoichiometric carbides and nitrides MX_y of groups IV and V transition d-metals is also the sum of several contributions [1, 2, 124]:

$$\chi = \chi_p^- + \chi_d^- + \chi_{VV\text{-}orb} + \chi_{pM}^+ + \chi_{dM}^+ + y(\chi_{pX}^+ + \chi_{dX}^+) , \tag{6}$$

where $\chi_{pM}^+ \equiv 0$ and $\chi_{pX}^+ \equiv 0$; the values of χ_{dM}^+ for Ti^{4+}, Zr^{4+}, Hf^{4+}, V^{5+}, Nb^{5+}, and Ta^{5+} are given in Section 1, and for C^{4+} and N^{5+}, the values of the core diamagnetism χ_{dX}^+ equal, respectively, -1.5×10^{-7} and -1.0×10^{-7} cm^3 mol^{-1} [52]. The difference between expressions (5) and (6) for the magnetic susceptibility of transition metals M and their nonstoichiometric compounds MX_y is not only that formula (6) contains an additional term that depends on the concentration of the nonmetal atoms X and takes into account the contribution of their ion cores but primarily that the energy distribution of density of electronic states in nonstoichiometric compounds differs strongly from the distribution in metals.

Of all the terms on the right-hand side of equation (6) only the Pauli paramagnetism term is temperature-dependent [125]:

$$\chi_p^-(T) = 2N_A\mu_B^2 N(E_F) + \frac{\pi^2 k_B^2}{3} N_A\mu_B^2\left\{N''(E_F) - \frac{[N'(E_F)]^2}{N(E_F)}\right\}T^2 , \tag{7}$$

where $N'(E_F)$ and $N''(E_F)$ are the values of the first and second energy derivatives of the density of electronic states at $E = E_F$. The Landau diamagnetism χ_d^- is proportional to the Pauli paramagnetism $\chi_p^-(0)$ at $T = 0$ K. If we extrapolate the measured susceptibility to $T = 0$ K and introduce corrections for the para- and diamagnetism of the ion cores, the resulting quantity $\chi^*(0)$ will be the sum of two paramagnetic contributions and one diamagnetic contribution: $\chi^*(0) = \chi_p^-(0) + \chi_d^-(0) + \chi_{VV\text{-}orb}$. Equation (7) suggests that at $T = 0$ K the Pauli paramagnetism directly depends only on the density of electronic states at the Fermi level, $N(E_F)$.

The magnetic susceptibility of NbC_y and TaC_y carbides decreases with diminishing carbon content and reaches its minimum for $NbC_{0.83}$ (see Fig. 10) and $TaC_{0.78}$ (see Fig. 12); the dependence of $\chi^*(0)$ on the composition of these carbides has the same shape. The Van Vleck orbital paramagnetism $\chi_{VV\text{-}orb}$ is always positive and can only increase as the deviation from stoichiometry for the disordered carbides

NbC_y and TaC_y grows, due to distortions in the symmetry of the immediate environment of the metal atoms and the essential nonsphericity of the electron wave functions. Hence, the observed reduction in the susceptibility of NbC_y and TaC_y carbides and the change of its sign as carbon content diminishes can be explained only by the changes in the magnitudes of the χ_p^- and χ_d^- contributions.

The electron energy spectrum of carbides of group V transition metals comprises two overlapping bands corresponding to the $M-C$ and $M-M$ interactions. The high-energy $M-M$ band is filled by less than one-half even in a stoichiometric carbide. If the carbide composition deviates from the stoichiometric one, the degree of the $M-M$ band filling changes and the density of electronic states at the Fermi level, $N(E_F)$, decreases [45, 126, 127]; the result is a decrease in χ_p^-. As we come nearer to the lower boundary of the homogeneity region, the $M-M$ band proves to be almost empty. According to Vonsovskii [125], the effective mass of collective electrons rapidly decreases with decreasing the energy band filling if the band is filled by less than one-half. This results in an increase in diamagnetism. The deviation in the composition of the NbC_y and TaC_y carbides from the stoichiometric one is also accompanied by a decrease in the effective mass of conduction electrons and, as a consequence, a rapid increase in the diamagnetism of the electron gas. When unfilled electron levels appear in the region where the $M-C$ and $M-M$ bands overlap, the effective electron mass begins to increase, while the diamagnetic contribution decreases. The result of such a change in the density of electronic states at the Fermi level, $N(E_F)$, and the effective electron mass m^* is a minimum in susceptibility corresponding to the region of overlap of the $M-C$ and $M-M$ bands. For the disordered NbC_y $(0.79 \leqslant y \leqslant 0.87)$ and TaC_y $(0.76 < y < 0.83)$ carbides, $\chi^*(0) = \chi_p^- + \chi_d^-$ is negative. This is possible if and only if the Landau diamagnetism χ_d^- of the conduction electrons in absolute value exceeds the Pauli paramagnetism χ_p^-. Since $\chi_d^- = -(m_0/m^*)^2\chi_p^-(0)/3$, we have $|\chi_d^-| > \chi_p^-$ if $m_0/m^* > \sqrt{3}$. Thus, the substantial diamagnetism of disordered nonstoichiometric niobium and tantalum carbides is caused by the small effective mass of the conduction electrons. On the whole, the variation in the magnetic susceptibility of disordered niobium and tantalum carbides is related to changes in the para- and diamagnetism of the conduction electrons.

The concentration dependence of the susceptibility $\chi(y)$ for the NbC_y carbide can be compared with the variation in the density of electronic states at the Fermi level, $N(E_F)$, as a function of the carbide's composition. Such a dependence was obtained by Marksteiner et al. [45], who used the Korringa–Kohn–Rostoker (KKR) coherent-potential (CP) approximation to calculate the band structure of the NbC_y carbide with varying carbon content. The researchers found that for NbC_y the dependence of $N(E_F)$ on y has a distinct minimum corresponding to the $NbC_{0.83}$ carbide. According to the band calculations done by Nemoshkalenko et al. [50] by the LCAO–CP (linear combination of atomic orbitals — the CP approximation) method, the minimum in $N(E_F)$ corresponds to the $NbC_{0.85}$ carbide. The results of Marksteiner et al. [45] and Nemoshkalenko et al. [50] are in good agreement with the experimental dependence $\chi(y)$ for disordered NbC_y carbide (see Fig. 10).

Let us now examine the nonstoichiometry effect on the magnetic susceptibility of disordered nonstoichiometric titanium and hafnium carbides TiC_y and HfC_y.

The magnetic susceptibility of the TiC_y and HfC_y carbides increases with decreasing carbon content y (see Figs 14 and 16); the values of $\chi^*(0)$ as functions of carbide composition change in a similar manner. The Van Vleck orbital paramagnetism $\chi_{\text{VV-orb}}$ is positive and, as the carbide composition deviates from the stoichiometric one, increases due to the distortion of the symmetry of the immediate environment of the metal atoms. The computations of the band structure of the TiC_y and ZrC_y carbides by the KKR–CP method in Refs [38, 45] showed that as the composition of the MC_y carbide deviates from the stoichiometric one, the distribution of the density of electronic states $N(E)$ changes: the curve $N(E)$ becomes less structured and all the peaks gradually smooth out. First and foremost, the $M-C$ band filling is reduced and the peaks, to which the p-electrons of the nonmetal contribute the most, diminish. Near the minimum in the density of states, vacancy peaks appear between the $M-C$ and $M-M$ bands, and these peaks are filled chiefly by electrons released by the $M-C$ bonds. The deviation from the stoichiometric composition and the emergence of vacancies have the least effect on the high-energy peaks which lie above the Fermi level, i.e., on the conduction band which is mainly metallic in nature. The Fermi level shifts a little toward lower energies, where the vacancy peaks are situated, and the density of states at the Fermi level, $N(E_F)$, increases [38, 45, 64, 128], which leads to an increase in $\chi_p^-(0)$. Although band structure calculations have never been conducted for hafnium carbide, basing our reasoning on the similarity between the titanium, zirconium, and hafnium carbides, we can assume that qualitatively the density of states $N(E)$ varies in the same way (as a function of the HfC_y composition) as that for TiC_y and ZrC_y and that deviation from stoichiometry is accompanied by an increase in $N(E_F)$. This agrees with the increase in the magnetic susceptibility of disordered hafnium carbide HfC_y as the carbon content decreases. The conduction $M-M$ band in carbides of group IV transition metals is filled by less than one-half, so that the variation of the extent of this filling is accompanied by an increase in the effective mass of collective electrons and, hence, by a decrease (in absolute value) in the Landau diamagnetism. Thus, when the composition of the TiC_y and HfC_y carbides deviates from the stoichiometric one to the lower boundary of the homogeneity region, the positive contributions $\chi_{\text{VV-orb}}$ and $\chi_p^-(0)$ increase, while the negative contribution χ_d^- decreases in absolute value; the consequence of all this is the observed general tendency of the magnetic susceptibility of the disordered TiC_y and HfC_y carbides to increase with decreasing y.

The presence of a segment in the $\chi(y, 300)$ curve for the disordered TiC_y carbide, where the susceptibility changes with composition $(0.59 \leqslant y \leqslant 0.63$; see Fig. 14) only slightly is an indication that in this region the density of states at the Fermi level, $N(E_F)$, depends very little on the carbide's composition. This agrees with the results of the numerical computation of the TiC_y electronic structure, done by Marksteiner et al. [38]. According to these results, the Fermi level in the stoichiometric $TiC_{1.00}$ carbide is located at the minimum of the density of states, i.e., within the region where the Ti–C and Ti–Ti subbands overlap; as the vacancy concentration $(1-y)$ increases from 0 to 0.5, the Fermi energy E_F decreases from 0.69 to 0.66 Ry (from 9.4 to 9.0 eV), while the density of electronic states at the Fermi level, $N(E_F)$, per unit cell increases from 5 to 23 Ry^{-1} (from 0.092 to 0.423 eV^{-1} form.u.^{-1}, or from 0.05 to

0.282 eV^{-1} atom^{-1}) (see Fig. 14). The increase in the vacancy concentration is accompanied by a smoothing-out of all the sharp peaks in the density of states (especially in the region below E_F), a decrease in the extent to which the low-energy band of Ti – C interactions is filled, a slight change in the shape of the high-energy band of Ti – Ti interactions, and the emergence of a minimum region for the density of states in the vacancy peak. This peak grows as the vacancy concentration increases, but in the process it becomes smeared. The curve representing the dependence of the density of states $N(E_F)$ on the relative content y of carbon in TiC_y and calculated in Ref. [38] contains a nearly horizontal section (see Fig. 14) with $N(E_F) \approx 15-17$ Ry^{-1} (0.152 – 0.192 eV^{-1} atom^{-1}) that corresponds to a range of compositions from $\mathrm{TiC}_{0.82}$ to $\mathrm{TiC}_{0.625}$, i.e., to the same range within which the concentration dependence of the magnetic susceptibility $\chi(y, 300)$ of disordered titanium carbide also contains a section that is nearly horizontal (see Fig. 14).

For disordered HfC_y with $y \geqslant 0.76$, the quantity $\chi^*(0) = \chi_p^-(0) + \chi_d^- + \chi_{\mathrm{VV\text{-}orb}}$ is negative (see Fig. 16). This is possible only if the Landau diamagnetism χ_d^- exceeds in absolute value the Pauli paramagnetism χ_p^-, i.e., if $m_0/m^* > \sqrt{3}$. Thus, the diamagnetism of the disordered HfC_y carbide for $y \geqslant 0.76$ is caused by the smallness of the effective mass of conduction electrons.

The diamagnetism of the nonstoichiometric NbC_y ($y < 0.9$), TaC_y ($y < 0.9$), and HfC_y ($y > 0.76$) carbides, which is caused by the large contribution to magnetic susceptibility from the diamagnetism of conduction electrons due to the smallness of the effective mass of these electrons, sets these carbides apart from transition metals, on the basis of which they were formed. Indeed, in transition metals the diamagnetism of the conduction electrons, which are s-electrons, is moderate [7]. As for d-electrons, they are highly localized in transition metals and thus play a very small role in conduction; moreover, d-electrons have a large effective mass.

The magnetic susceptibility of zirconium carbide ZrC_y monotonically decreases with an increase in carbon content in the carbide (see Fig. 5). This result agrees with the results of calculations of the ZrC_y band structure, carried out by Marksteiner et al. [45], according to which the density of electronic states at the Fermi level, $N(E_F)$, drops from 0.33 to 0.09 eV^{-1} $\mathrm{form.u.}^{-1}$ (or from 17.8 to 5.1 Ry^{-1} per unit cell) in going from $\mathrm{ZrC}_{0.60}$ to $\mathrm{ZrC}_{1.00}$. In the case of zirconium nitride ZrN_y, the same calculation revealed the presence of a maximum in $N(E_F)$, corresponding to the $\mathrm{ZrN}_{0.65}$ nitride. No extrema were detected in the experimental curve representing the dependence $\chi(y, 300)$ for zirconium nitride [65] (see Fig. 5). However, if we allow for the data given in Ref. [45] and the general ideas concerning the electron energy spectrum of nonstoichiometric compounds MX_y with the cubic structure $B1$, the curve $\chi(y)$ should contain an extremum for $y < 0.8$.

Overall, the above data suggest that the nonstoichiometry effect on the magnetic susceptibility of carbides and nitrides of transition d-metals can be consistently explained by the transformation of the electron energy spectrum for these compounds.

5. Short- and long-range order

What are the causes for the observed reduction in the magnetic susceptibility of the nonstoichiometric NbC_y, TaC_y, HfC_y, and TiC_y carbides, which accompanies ordering?

The reduction of susceptibility that accompanies ordering becomes possible if the effective mass of a collective electron in an ordered carbide is smaller than in a disordered one, i.e., when $m^*_{\mathrm{ord}} < m^*_{\mathrm{disord}}$. If the change in the effective mass of conduction electrons in the ordering process is small, the decrease in susceptibility can be attributed to the change in the density of electronic states at the Fermi level, $N(E_F)$. However, for niobium carbide, the value of $N(E_F)$ changes very little in the ordering process [48, 129, 130], so there is no reason to believe that the situation is different in tantalum, titanium, and hafnium carbides. Thus, the decrease in the density of electronic states at the Fermi level can be excluded as the reason for the decrease in the susceptibility χ of carbides undergoing disorder – order transitions.

The most plausible reason for the decrease in susceptibility of carbides undergoing ordering is a change in the contribution of orbital paramagnetism, related to formation of short-range order [60, 94]. Short-range order is sure to appear where long-range order is formed, i.e., under ordering. Such short-range order has become known as superstructural short-range order (see Refs [131, 132]).

The magnetic susceptibility of nonstoichiometric compounds MX_y with a $B1$ basis structure is determined chiefly by the electron subsystem of the metal atoms. In disordered nonstoichiometric carbides there is no short-range order, and the immediate environment of a metal atom may exhibit different types of symmetry, while in ordered carbides only several (usually only one) types of the immediate environment of metal atoms can exist. Since the position-averaged symmetry of the immediate environment of metal atoms is higher in ordered carbides than in disordered ones, the contribution of the Van Vleck orbital paramagnetism to the susceptibility of ordered carbides is smaller in magnitude than a similar contribution into χ of disordered carbides. One confirmation of the symmetry effect of the immediate environment on the size of the magnetic susceptibility is provided by the results of calculating the parameters of short-range order that lean upon the experimental data on magnetic susceptibility; a method for such calculations has been developed in Refs [60, 86, 133].

The experimental dependences $\chi(y, T)$ for carbides MC_y from 300 K to the temperature at which the disorder – order or order – disorder transition begins are described by a function of the following form

$$\chi(y, T) = a(y) + b(y)T^2 , \tag{8}$$

which corresponds to the temperature dependence of the Pauli paramagnetism (7).

In Refs [60, 86, 133], the crystal lattice of the nonstoichiometric compound MX_y with the cubic structure $B1$ is thought of as a set of noninteracting clusters P_i in the form of octahedrons consisting of six filled or vacant sites of the nonmetallic sublattice with a metal atom at its center. In Refs [1, 2, 124, 133, 134], it is shown that such an octahedral cluster makes it possible to take into account interatomic metal – nonmetal interactions, which are the most important interactions in strongly nonstoichiometric compounds, the multiparticle correlations in the first coordination sphere of a metal atom, and absolutely all the sites of the crystal lattice. In a disordered compound MX_y, the interstitial atoms and the vacancies are distributed statistically, with the result that cluster probabilities $P_i(y)$ depend solely on the compound's composition and are described by a binomial distribution; the probability of clusters containing n vacancies and $6-n$ interstitial atoms is defined as follows:

$$P_i(y) = P_i^{\text{bin}}(y) = y^{6-n}(1-y)^n \,. \tag{9}$$

If we express the magnetic susceptibility (8) of a disordered carbide in terms of the susceptibilities $\chi_i = a_i + b_i T^2$ of individual clusters as

$$\chi(y, T) = \sum_i \chi_i(T)\lambda_i P_i(y) \,, \tag{10}$$

then, knowing the probability $P_i(y)$ and the experimental coefficients $a(y)$ and $b(y)$ for several disordered carbides with a different content of nonmetal interstitial atoms, we can calculate the coefficients a_i and b_i for each cluster [λ_i in expansion (10) is the number of equivalent configurations of a cluster in which n sites out of six are vacant and which has the ith configuration of the relative positions of atoms and vacancies]. Indeed, combining equations (8) and (10), we get

$$\chi(y, T) = \sum_i (a_i + b_i T^2)\lambda_i P_i(y) \,, \tag{11}$$

whence

$$a(y) = \sum_i a_i \lambda_i P_i(y) \,, \qquad b(y) = \sum_i b_i \lambda_i P_i(y) \,. \tag{12}$$

Introducing the calculated values of $P_i(y) = P_i^{\text{bin}}(y)$ into Eqn (12) written for the disordered compound MX_y, we can find the coefficients a_i and b_i. Then, using the experimental coefficients $a(y)$ and $b(y)$ for the ordered nonstoichiometric compound, the obtained values of the coefficients a_i and b_i, and the normalization conditions $\sum_i \lambda_i P_i(y) = 1$ and $\sum_i \ell_i \lambda_i P_i(y) = y$ (here, $\ell_i = (6-n)/6$ is the fraction of sites occupied by carbon atoms in a cluster with the ith configuration), we can calculate the cluster probabilities $P_i^{\text{ord}}(y)$ in the ordered nonstoichiometric compound.

The short-range order parameters α_1 and α_2 for the first and second coordination spheres of the nonmetallic sublattice (the carbon sublattice in the case of carbides) can be found by the formula

$$\alpha_j = 1 - \frac{P_{X-\square}^{\text{ord}\,(j)}}{P_{X-\square}^{\text{bin}}} \,, \tag{13}$$

where $P_{X-\square}^{\text{bin}} = \lambda_{X-\square}\, y(1-y)$ is the binomial carbon atom–vacancy ($X-\square$) pair formation probability ($\lambda_{X-\square} = 2$) corresponding to the disordered state of the MC_y carbide and depending only on the carbide's composition. The probabilities of forming pairs $X-\square$ in any jth coordination sphere of the nonmetallic sublattice of the ordered compound are defined as follows:

$$P_{X-\square}^{\text{ord}\,(j)} = \sum_i n_i^{(j)} \lambda_i P_i^{\text{ord}}(y) \,, \tag{14}$$

where $n_i^{(j)}$ is the relative fraction of the carbon atom–vacancy pairs in the jth coordination sphere of a cluster with the ith configuration. For the case of an octahedral cluster, the values of the coefficients λ_i, ℓ_i, and $n_i^{(j)}$ for nonstoichiometric compounds with the cubic structure $B1$ can be found in Refs [1, 2, 55].

According to Refs [133, 134], to achieve a correct description of nonstoichiometric MX_y compounds with $0.7 \leqslant y \leqslant 1.0$, we need only take into account four configurations of the octahedral cluster: a 'complete' cluster (not containing vacancies) with the probability P_0; a cluster with one vacancy and the probability P_1, and clusters with two nonadjacent and two adjacent vacancies with the probabilities P_2 and P_3. Titanium carbide TiC_y has a homogeneity region that is wider than those of niobium, tantalum, and hafnium carbides, so its meaningful description in the interval $0.5 \leqslant y \leqslant 1.0$ requires allowing for eight configurations of the octahedral cluster [1, 2]: the four earlier-described configurations with probabilities P_0, P_1, P_2, and P_3; clusters containing three vacancies each, with probabilities P_4 and P_5, and also clusters containing four vacancies each, with probabilities P_6 and P_7.

Equation (8) was used in Refs [55, 57, 60, 86, 94] together with the experimental $\chi(y, T)$ curves for finding the coefficients a and b for the NbC_y, TaC_y, TiC_y, and HfC_y carbides of different compositions in the disordered and ordered states and then to calculate the cluster probabilities $P_i(y)$ in ordered carbides. Equations (13) and (14) were then used to estimate the short-range order parameters α_1 and α_2. These parameters for the ordered NbC_y, TaC_y, TiC_y, and HfC_y carbides are listed in Table 2.

Comparison of the calculated values of α_1 and α_2 with the theoretically determined short-range order parameters for all superstructures whose formation is possible in nonstoichiometric interstitial compounds provides the means for making an assumption concerning the type and symmetry of the resultant ordered phases of the niobium, tantalum, hafnium, and titanium carbides. The idea of comparing the short- and long-range order parameters and the method used for estimating the long-range order parameter were first developed in studies of the magnetic susceptibility of titanium and hafnium carbides [55, 57, 89–92].

In niobium and tantalum carbides, and also in the $\text{TiC}_{0.81}$ and $\text{HfC}_{0.83}$ carbides, the two short-range order parameters α_1 and α_2 are negative, are close in absolute value, and are greater than -0.2. This combination of the parameters α_1 and α_2 corresponds to a superstructure of the $M_6\text{C}_5$ type with a monoclinic or trigonal symmetry [131, 132]. In the $\text{HfC}_{0.71}$ and $\text{HfC}_{0.78}$ carbides, $\alpha_1 < 0$ and $\alpha_2 \approx 0$. This combination of the parameters α_1 and α_2 is possible only in an ordered phase of the $M_3\text{C}_2$ type with an orthorhombic (space group *Immm*) or monoclinic (space group *P*2) structure [131, 132].

In the $\text{TiC}_{0.50}$, $\text{TiC}_{0.55}$, and $\text{Ti}_{0.59}$ carbides, $\alpha_1 \approx 0$ and $-1 < \alpha_2 < -0.65$. This combination of the parameters α_1 and α_2 is possible only in the ordered phase Ti_2C with a trigonal (space group $R\bar{3}m$) or cubic (space group $Fd\bar{3}m$) symmetry. Indeed, in these Ti_2C superstructures of stoichiometric composition ($y_{\text{st}} = 1/2$), the limiting values of the short-range order parameters $\alpha_1(y_{\text{st}}, \eta_{\max})$ and $\alpha_2(y_{\text{st}}, \eta_{\max})$ are equal to 0 and -1, respectively [1, 2]. In the $\text{TiC}_{0.63}$, $\text{TiC}_{0.68}$, and $\text{TiC}_{0.69}$ carbides, the both short-range order parameters are negative ($-0.06 \leqslant \alpha_1 \leqslant -0.01$, $\alpha_2 \approx -0.4$), which is possible only with the formation of a rhombic (space group $C222_1$) superstructure of the $M_3\text{C}_2$ type [1,2]. For this superstructure we always have $\alpha_2 < \alpha_1 < 0$, and with the stoichiometric composition ($y_{\text{st}} = 2/3$) the limiting values of the parameters $\alpha_1(y_{\text{st}}, \eta_{\max})$ and $\alpha_2(y_{\text{st}}, \eta_{\max})$ are $-1/8$ and $-1/2$, respectively.

The following formula describe the relationship between the parameters α_j of superstructure short-range order and the long-range order parameter η in the nonmetallic sublattice of

Table 2. Parameters of short-range order in the ordered nonstoichiometric TiC_y, HfC_y, NbC_y, and TaC_y carbides determined through magnetic susceptibility measurements [55, 57, 60, 94].

Composition	Experimental short-range order parameters		Type and space group of the ordered phase	Theoretical short-range order parameters in the ideal ordered phase		Maximum theoretical long-range order parameter η_{max}	Experimental long-range order parameter η
	$\alpha_1 \pm 0.005$	$\alpha_2 \pm 0.005$		α_1	α_2		
$NbC_{0.81}$	−0.153	−0.137	Nb_6C_5 ($C2/m$)	−0.2	−0.2	0.97	0.87 – 0.92
$NbC_{0.83}$	−0.132	−0.126	Nb_6C_5 ($C2/m$)	−0.2	−0.2	0.996	0.80 – 0.82
$NbC_{0.88}$	−0.064	−0.040	Nb_6C_5 ($C2/m$)	−0.2	−0.2	0.72	0.39 – 0.49
$TaC_{0.82}$	−0.080	−0.086	Ta_6C_5 ($C2/m$?)	−0.2	−0.2	0.984	0.65 – 0.68
$TaC_{0.83}$	−0.063	−0.080	Ta_6C_5 ($C2/m$?)	−0.2	−0.2	0.996	0.57 – 0.64
$TaC_{0.85}$	−0.059	−0.043	Ta_6C_5 ($C2/m$?)	−0.2	−0.2	0.90	0.44 – 0.52
$TiC_{0.50}$	0	−0.793	Ti_2C ($R\bar{3}m, Fd\bar{3}m$)	0	−1.0	1.00	0.89
$TiC_{0.55}$	0	−0.700	Ti_2C ($R\bar{3}m, Fd\bar{3}m$)	0	−1.0	0.90	0.83
$TiC_{0.59}$	0.004	−0.668	Ti_2C ($R\bar{3}m, Fd\bar{3}m$)	0	−1.0	0.82	0.80
$TiC_{0.63}$	−0.055	−0.406	Ti_3C_2 ($C222_1$)	−0.125	−0.5	0.945	0.68 – 0.92
$TiC_{0.68}$	−0.053	−0.394	Ti_3C_2 ($C222_1$)	−0.125	−0.5	0.96	0.64 – 0.88
$TiC_{0.69}$	−0.011	−0.441	Ti_3C_2 ($C222_1$)	−0.125	−0.5	0.93	0.29 – 0.92
$TiC_{0.81}$	−0.093	−0.096	Ti_6C_5 ($C2/m, P3_1, C2$)	−0.2	−0.2	0.972	0.72 – 0.73
$HfC_{0.71}$	−0.207	−0.001	M_3C_2 ($P2, Immm$)	−0.25	0	0.87	0.88
$HfC_{0.78}$	−0.123	−0.001	M_3C_2 ($P2, Immm$)	−0.25	0	0.66	0.62
$HfC_{0.83}$	−0.079	−0.023	M_6C_5 ($C2/m, P3_1, C2$)	−0.2	−0.2	0.996	0.34 – 0.63

the MC_y compound:

$$\alpha_j(y, \eta) = -\frac{\eta^2 (1 - y_{st})(m_{21}^{(j)} - y_{st})}{y(1 - y)} , \qquad (15)$$

where $m_{21}^{(j)}$ is a coefficient equal to the relative number of occupied sites in the jth coordination sphere with a vacant site as its center. For superstructures of the M_2C type with space groups $R\bar{3}m$ and $Fd\bar{3}m$, the values of the coefficients $m_{21}^{(j)}$ in the first and second coordination spheres are 1/2 and 1, respectively; for superstructures of the M_3C_2 type with space groups *Immm* and *P*2, $m_{21}^{(1)} = 5/6$ and $m_{21}^{(2)} = 2/3$; for superstructures of the M_3C_2 type with the space group $C222_1$, these values are 3/4 and 1, respectively, and, finally, for superstructures of the M_6C_5 type with space groups $C2/m$, $P3_1$, and $C2$, both coefficients are equal to 1 [2].

The parameters α_1 and α_2 found from magnetic susceptibility measurements characterize the total (the superstructural and the correlational) short-range order. If we assume that the contribution of the correlation short-range order is negligible, we can use formula (15) for estimating the long-range order parameter η in the samples of niobium, tantalum, hafnium, and titanium carbides after measuring their susceptibilities. The calculations of η for the $HfC_{0.71}$ and $HfC_{0.78}$ carbides, done in Ref. [57], used the values of the short-range order parameter α_1 in the first coordination sphere, since in the ordered M_3C_2 phase (space groups *Immm* and *P*2) the parameter $\alpha_2 \equiv 0$ and is independent of η. To calculate the long-range order parameter for the $TiC_{0.50}$, $TiC_{0.55}$, and $TiC_{0.59}$ carbides, Zueva et al. [55] used the values of the short-range order parameter α_2 in the second coordination sphere, since for the ordered Ti_2C phase (space groups $R\bar{3}m$ and $Fd\bar{3}m$) the parameter α_1 does not depend on η. The calculations of η for other carbides leaned upon the short-range order parameters in the first and second coordination spheres. The values of η estimated on the basis of experimental data proved to be smaller than the theoretically possible maximum value η_{max} of the long-range order parameter in completely ordered carbides (see Table 2). The maximum value of the long-range order parameter in one ordered phase or another depends only on the type of the $M_{2t}X_{2t-1}$ superstructure and the composition of the ordering compound MX_y, and it is defined as follows [1, 2]:

$$\eta_{max}(y) = \begin{cases} 2t(1 - y) & \text{for } y \geqslant \dfrac{2t - 1}{2t} , \\ \dfrac{2ty}{2t - 1} & \text{for } y < \dfrac{2t - 1}{2t} . \end{cases} \qquad (16)$$

Thus, the samples that have been investigated exhibit a high (but not the highest) degree of ordering for nonstoichiometric carbides.

The temperature dependences of the susceptibility $\chi(T)$ of the nonstoichiometric disordered and ordered NbC_y, TaC_y, TiC_y, and HfC_y carbides, reported in Refs [55, 57, 60, 86 – 94], the disorder – order transformation temperatures obtained from these data, and the conclusions about the superstructures that form in these carbides — all agree fairly well with the phase diagrams of the Nb – C, Ta – C, Ti – C, and Hf – C systems [1 – 4, 107, 109, 135].

Thus, the method developed in Refs [60, 86] makes it possible to quantitatively estimate the short- and long-range order parameters from the data on the temperature dependences of the magnetic susceptibility of nonstoichiometric compounds, i.e., to extract information about the fine features of the crystal structures for these compounds. A remark is in order here. The method of analyzing magnetic susceptibility [60, 86] is based on the assumption that there is no short-range order in disordered nonstoichiometric compounds. However, even at temperatures exceeding the order – disorder transition temperature T_{trans}, when the long-range order disappears, the short-range order remains. This fact is corroborated by, say, the results of investigating the short-range order in the disordered titanium, vanadium, and niobium carbides by the method of diffuse scattering of electrons or neutrons [136 – 141]. Hence, for a more correct estimation of short-range order parameters on the basis of the results of magnetic susceptibility measurements, we must allow for the short-range order that exists in the disordered phase, order that can be determined through additional experiments on elastic neutron scattering.

6. Magnetic susceptibility of nonstoichiometric titanium monoxide

In Section 2 we examined the stoichiometry effect on the magnetic susceptibility of cubic titanium monoxide TiO_y on the basis of earlier research [78–82]. The most reliable results for the magnetic susceptibility of properly certified disordered cubic titanium monoxide TiO_y $(0.920 \leqslant y \leqslant 1.262)$ have recently been reported in Refs [83, 84]. The unique nature of the crystal structure (the presence of a double imperfection) and a behavior of the magnetic susceptibility that sets this monoxide apart from other nonstoichiometric compounds require a separate discussion of the properties of this compound.

Measurements of the electrical conductivity of TiO_y samples at 4.2 and 77–300 K [83, 84] have shown that, depending on oxygen content, titanium monoxide may be either an (electron) conductor or a semiconductor. However, the narrow temperature range for measuring the conductivity did not make it possible to reliably estimate the band gap of the TiO_y monoxides with $y \geqslant 1.087$. To determine the band gap and to get a more detailed idea about the electronic structure of TiO_y, the researchers studied the magnetic susceptibility of this oxide [83, 84].

The magnetic susceptibility χ of the disordered titanium monoxide TiO_y $(0.920 \leqslant y \leqslant 1.262)$ was measured in the temperature range from 4.2 to 400 K in 8.8-, 25-, 30-, and 50-kOe magnetic fields. The susceptibility of $TiO_{0.946}$, $TiO_{1.069}$, $TiO_{1.087}$, and $TiO_{1.262}$ samples was additionally measured in a temperature interval from 300 K to the temperature (about 1000 K) at which the disorder–order transition begins.

Measurements of the magnetization M in magnetic fields H up to 50 kOe at 4, 130, and 300 K have shown that the studied samples of the TiO_y monoxides had no remanent magnetization. This means that the TiO_y samples contained no ferromagnetic impurities. At all the indicated measurement temperatures, TiO_y $(0.920 \leqslant y \leqslant 1.262)$ proved to be a weak paramagnet, and at $T = 300$ K the magnetic susceptibility increased from 0.95×10^{-6} cm^3 g^{-1} for $TiO_{1.262}$ to 1.75×10^{-6} cm^3 g^{-1} for $TiO_{0.920}$ as oxygen content decreased, which is in good agreement with the results obtained by Denker [79] and Vasil'ev et al. [80].

Magnetic susceptibility measurements have demonstrated that for all the TiO_y samples under investigation the temperature dependences $\chi(T)$ (Figs 18 and 19) contain two sections with opposite directions of variation of χ as a function of temperature. The decrease in magnetic susceptibility on the low-temperature section ($T < 150$–200 K) is a characteristic property of the paramagnetic component which is described by a modified Curie law $\chi(T) = \chi(0) + C/(T + \varDelta)$ with a temperature-independent paramagnetic contribution $\chi(0)$ and $\varDelta > 0$. For temperatures above 150–200 K, the susceptibility $\chi(T)$ incorporates, in addition to the contribution $\chi(0) + C/(T + \varDelta)$, a linear, quadratic, or more composite functions of temperature.

The Curie paramagnetism per unit mass of substance is described by the formula

$$\chi = \frac{n_m N_A}{M} \frac{(p\mu_B)^2}{3k_B T} \equiv \frac{C}{T},$$

where n_m is the relative concentration of atoms having a magnetic moment, $\mu_{eff} = p\mu_B$ is the effective magnetic moment, and M is the molecular mass. This formula yields $p^2 = (CM/n_m)(3k_B/N_A\mu_B^2)$, or (with allowance for the values of N_A, μ_B, and k_B) $p \approx \sqrt{8CM/n_m}$, where the Curie constant C has the dimension [cm^3 K g^{-1}]. If the concentration n_m of atoms possessing magnetic moments is unknown, the magnetic moment averaged over all atoms is defined as $p_{av} \approx \sqrt{8CM}\,\mu_B$. Note that for estimating the values of p and p_{av} properly we must utilize the molecular mass M corresponding to the real composition of titanium monoxide with allowance for the presence of vacancies in each sublattice, i.e., Ti_xO_z.

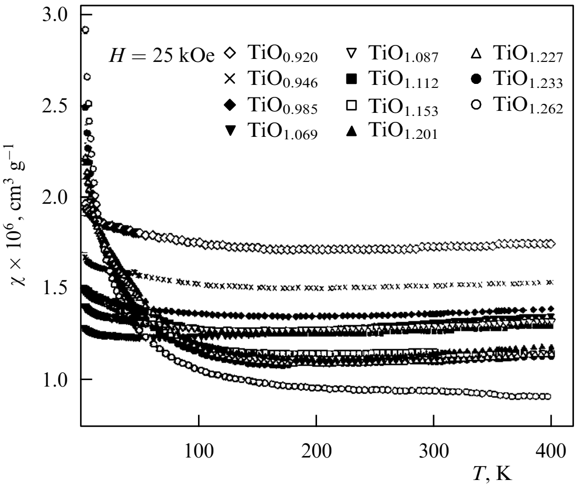

Figure 18. Magnetic susceptibility χ of disordered cubic titanium monoxides TiO_y with varying oxygen content in the temperature range from 4.0 to 400 K (the magnetic field strength in the measurements conducted was $H = 25$ kOe) [83, 84].

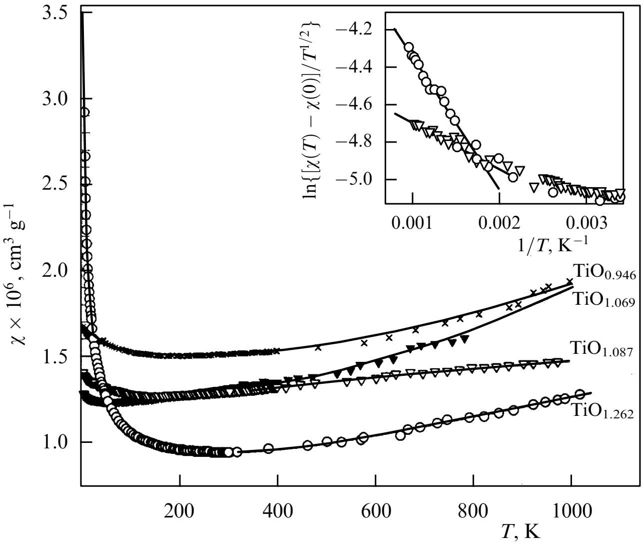

Figure 19. Magnetic susceptibility χ of the titanium monoxides $TiO_{0.946}$, $TiO_{1.069}$, $TiO_{1.087}$, and $TiO_{1.262}$ in the temperature range from 4 K to the temperature (about 1000 K) of the beginning of the disorder ↔ order transition [83, 84]. The inset depicts the behavior of the high-temperature susceptibility of the monoxides $TiO_{1.087}$ and $TiO_{1.262}$, plotted in the $(\ln\{[\chi(T) - \chi(0)]/T^{1/2}\}, 1/T)$ plane.

The calculations done in Refs [83, 84] with the use of the found values of C have shown that the effective magnetic moment averaged over all atoms, μ_{eff}, amounts to 0.015–

Table 3. Parameters of functions (17), (20), and (21) that describe the magnetic susceptibility χ and some magnetic characteristics of disordered cubic titanium monoxide TiO_y [84].

TiO_y	Function	Temperature interval, K	Parameters						
			$\chi(0) \times 10^6$, $cm^3\ g^{-1}$	$C \times 10^6$, $cm^3\ K\ g^{-1}$	$\varDelta$, K	$b \times 10^{12}$, $cm^3\ K^{-2}\ g^{-1}$	$a \times 10^9$, $cm^3\ K\ g^{-1}$	ΔE, eV	p_{av}
$TiO_{0.920}$	(17)	4.0–400	1.629	17.9	55.0	0.501	—	—	0.089
$TiO_{0.946}$	(17)	4.0–1000	1.410	22.9	88.6	0.493	—	—	0.100
$TiO_{0.985}$	(17)	4.0–400	1.290	10.7	55.4	0.469	—	—	0.069
$TiO_{1.069}$	(17)	4.0–1000	1.237	0.54	8.5	0.659	—	—	0.015
$TiO_{1.087}$	(20)	4.0–1000	1.196	14.9	71.8	—	—	0.061	0.081
$TiO_{1.112}$	(21)	4.0–400	1.059	44.9	96.0	—	0.889	—	0.225
$TiO_{1.153}$	(21)	4.0–400	0.909	56.4	89.7	—	0.898	—	0.224
$TiO_{1.201}$	(21)	4.0–400	0.798	58.3	39.5	—	1.243	—	0.195
$TiO_{1.227}$	(21)	4.0–400	0.806	51.7	34.6	—	1.025	—	0.178
$TiO_{1.233}$	(21)	4.0–400	0.917	28.1	14.5	—	0.578	—	0.118
$TiO_{1.262}$	(20)	4.0–1000	0.847	24.1	7.8	—	—	0.173	0.101

$0.225\,\mu_B$ (Table 3). The small value of μ_{eff} is an indication that the Curie contribution to magnetic susceptibility is likely to be from impurities. Probably, the majority of the Ti^{2+} ions in TiO_y have paired electrons or there is exchange cation–cation interaction in the monoxide. The electron paramagnetic resonance (EPR) method was unable to determine in TiO_y the presence of any ions with uncompensated magnetic moments due to the high concentration of delocalized electrons. Since the TiO_y samples contained no ferromagnetic impurities, the presence of a small effective magnetic moment may be caused by the Ti^{2+} and Ti^{3+} ions having an impurity nature. Judging by the value of p_{av}, the content of such impurities varies from 2 to 8 at.%. The Curie paramagnetism manifests itself most vividly in titanium monoxides TiO_y with relatively high oxygen content $y > 1.2$ (see Fig. 19).

The temperature dependence $\chi(T)$ for titanium monoxides TiO_y with $y \leqslant 1.069$ (see Figs 18 and 19) in the entire investigated interval of temperatures (4.2–400 K or 4.2–1000 K) was described with high accuracy by the function

$$\chi(T) = \chi(0) + \frac{C}{T + \varDelta} + bT^2 . \tag{17}$$

The presence of the quadratic term bT^2 is a characteristic property of the Pauli paramagnetism for conduction electrons, which agrees with the metallic type of conduction in these monoxides.

For TiO_y monoxides with $y \geqslant 1.087$, the temperature dependences of the magnetic susceptibility are more complicated, which is especially evident in the high-temperature region (see Fig. 19). If the charge carriers in TiO_y obey the Boltzmann statistics and the charge carrier concentration in TiO_y with $y \geqslant 1.087$ is described for $T > 300$ K by the formula

$$n_e = 2(m^*)^{3/2} \left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2} \exp\left(-\frac{\Delta E}{2k_B T}\right), \tag{18}$$

then, in accordance with the Curie formula $\chi_p(T) = n_e(\mu_B)^2/k_B T$, the part of the magnetic susceptibility that is temperature-dependent will have a paramagnetic component

$$\chi_p(T) = 2\left(\frac{m^*}{2\pi\hbar^2}\right)^{3/2} k_B^{1/2} \mu_B^2 T^{1/2} \exp\left(-\frac{\Delta E}{2k_B T}\right)$$
$$\equiv A T^{1/2} \exp\left(-\frac{\Delta E}{2k_B T}\right), \tag{19}$$

where

$$A = 2\left(\frac{m_0}{2\pi\hbar^2}\right)^{3/2} k_B^{1/2} \mu_B^2 \left(\frac{m^*}{m_0}\right)^{3/2}$$
$$= 3.008 \times 10^{-9} \left(\frac{m^*}{m_0}\right)^{3/2} \ [K^{-1/2}],$$

m_0 is the electron mass, m^* is the effective mass of the charge carriers, and ΔE is an energy parameter that has the meaning of activation energy and in the case of intrinsic conduction is equal to the band gap E_g between the valence and conduction bands. Note that formula (19) describes the dimensionless magnetic susceptibility per unit volume. With allowance for these features of the temperature dependence $\chi(T)$ and the fact that $A_m = A/d$ (d is the density), the researchers approximated the measured mass magnetic susceptibility of the titanium monoxides TiO_y with $y \geqslant 1.087$ in the temperature range between 4.2 and 1000 K by the function [83, 84]

$$\chi(T) = \chi(0) + A_m T^{1/2} \exp\left(-\frac{\Delta E}{2k_B T}\right) + \frac{C}{T + \varDelta} \tag{20}$$

which allows for the temperature-independent contribution $\chi(0)$, Pauli's paramagnetic contribution for the electron system with an energy gap, and Curie's paramagnetic contribution. For $T < 400$ K, the second term on the right-hand side of equation (20) can be replaced by a term aT linear in temperature, with the result that magnetic susceptibility of the TiO_y monoxides with $y \geqslant 1.087$ was described on the temperature interval from 4.0 to 400 K by the following formula

$$\chi(T) = \chi(0) + \frac{C}{T + \varDelta} + aT . \tag{21}$$

The numerical values of the parameters of the functions (17), (20), and (21) used in Refs [83, 84] for approximating the temperature dependence $\chi(T)$ for the studied titanium monoxides TiO_y are listed in Table 3.

According to the estimation made in Refs [83, 84], the effective mass of charge carriers in the $TiO_{1.087}$ and $TiO_{1.262}$ monoxides amounts to roughly $7m_0$ and $14m_0$, respectively. This fairly large effective mass corroborates the admissibility of using the Boltzmann distribution to describe the carrier concentration in the TiO_y monoxides with $y \geqslant 1.087$.

For the $TiO_{1.087}$ and $TiO_{1.262}$ monoxides, the values of ΔE found from formula (20) are 0.061 and 0.173 eV, respectively.

The values of ΔE determined for the same monoxides from the temperature dependences of conduction are 0.028 and 0.032 eV, respectively [83, 84]. It can be assumed that the values of ΔE found from the low-temperature dependences of conduction correspond to the activation energy of impurity levels, while the values of ΔE obtained for a wider temperature range from the magnetic susceptibility determine the band gap in the case of intrinsic conduction. The small value of the band gap enabled the authors of Refs [83, 84] to consider the titanium monoxide TiO_y with $y \geqslant 1.087$ a narrow-gap semiconductor.

On the whole, the results obtained in Refs [83, 84] suggest that as oxygen content grows, a narrow gap between the valence and conduction bands appears in the electronic structure of disordered cubic titanium monoxide TiO_y. In accordance with this, titanium monoxide TiO_y may behave like a d-metal or like a semiconductor, depending on oxygen content. This means that as oxygen content in the disordered monoxide TiO_y rises, i.e., as the concentration of the oxygen vacancies decreases and, simultaneously, the concentration of titanium vacancies increases, a metal – semiconductor transition can be observed in experiments.

The high concentration of vacancies in the titanium and oxygen sublattices of TiO_y is a prerequisite for ordering. In view of this, it would be interesting to study the magnetic properties of ordered nonstoichiometric titanium monoxide.

7. Conclusions

Analysis of the experimental data on the magnetic susceptibility of such nonstoichiometric MX_y compounds as the cubic carbides, nitrides, and oxides of transition d-metals first of all shows how little we know about these compounds. Indeed, even variations in magnetic susceptibility, depending on the nonstoichiometry of these compounds which have very wide homogeneity regions, have been studied more or less systematically mainly for carbides and monoxides. However, a large part of these studies has been done without accounting for the real structural state of these compounds, which can be disordered or ordered with different degrees of long-range order. The study of the magnetic susceptibility in a broad temperature range encompassing the temperature region within which structural phase transitions of the order – disorder or disorder – order type are possible in nonstoichiometric compounds, has so far been done only with carbides.

Despite the obvious gaps, research over the last 15 to 20 years into the magnetic properties of strongly nonstoichiometric ordering compounds has shown that magnetic susceptibility measurements not only make it possible to establish the magnitude and sign of the susceptibility of these weakly magnetic substances but are also sensitive to fine changes in the electronic structure caused by ordering. Measurements of the temperature dependence of magnetic susceptibility also make it possible to determine the temperature of a nonequilibrium irreversible transition from a quenched disordered state to an equilibrium ordered state and the temperature of an equilibrium reversible order – disorder transition. The way the susceptibility changes in the region of the equilibrium reversible order – disorder transition may serve as an indication of the order of the phase transformation.

We have shown in this review that studies of the temperature and concentration dependences of the magnetic susceptibility of nonstoichiometric compounds can be used in analyzing short-range order in the nonmetallic sublattice of such compounds. In this case, the comparison of the susceptibility of the same compound in the disordered and ordered states makes it possible to estimate the nature of the immediate environment of metal atoms M, an environment consisting of nonmetal atoms and structural vacancies, and in this way to establish what short-range order is present in the nonmetallic sublattice. Comparison of the established short-range order parameters with the parameters corresponding to the possible ordered phases of the nonstoichiometric compounds makes it possible to determine, with a high degree of confidence, the type of a new superstructure and, in some cases, even the symmetry of this superstructure. Numerical analysis of the short-range order parameters found from susceptibility measurements is the instrument with which we can also determine the degree of long-range order in nonstoichiometric compounds MX_y. Thus, experimental studies of the magnetic susceptibility allow us to extract information about the electronic structure, as well as about the crystal structure of nonstoichiometric compounds. The magnetic susceptibility method can be used for studying short-range order not only in carbides (which were largely considered here) but also in other compounds with an extended homogeneity region and in substitutional solid solutions.

At the same time, one must bear in mind that the data on short-range order in ordered nonstoichiometric carbides, extracted from magnetic susceptibility measurements, may be used only for estimating the short-range order parameters. Indeed, the assumption that in quenched disordered nonstoichiometric compounds there is ideal disorder and, therefore, the cluster formation probabilities in a disordered compound can be described by a binomial distribution is not quite true. For instance, studies of short-range order in disordered carbides by the method of diffuse scattering of electrons or neutrons have shown that the short-range order in these compounds is retained at least in the three nearest coordination spheres even at a temperature that is 200 K higher than the order – disorder transition temperature. To determine how accurately the magnetic susceptibility method estimates the short-range order parameters, parallel experiments are needed in which the magnetic susceptibility and the elastic diffuse scattering of neutrons will be studied using the same samples of a nonstoichiometric compound in disordered and ordered states. The short-range order parameters for the disordered compound, found from diffuse scattering, should be used in calculations of the cluster probabilities P_i in the disordered compound and in subsequent calculations of the susceptibilities χ_i of individual clusters. This increases the accuracy of determining the cluster probabilities and short-range order parameters for the ordered nonstoichiometric compound. Comparison of the short-range order parameters for an ordered carbide, found from magnetic susceptibility measurements and from experiments in diffuse scattering, will show how justified the use of the magnetic susceptibility method is in studying short-range order in the distribution of interstitial atoms and vacancies.

So far, no such an experiment has been conducted, and we are forced to limit ourselves to comparing data on short-range order in nonstoichiometric carbides obtained, on the one hand, from magnetic susceptibility and, on the other, from NMR and diffuse neutron scattering. The scientific literature contains such data only for niobium and titanium carbides. Such a comparison [142] shows that the short-range order in

NbC_y, found by the magnetic susceptibility method [60, 86], agrees well with the results of NMR studies [143, 144] and neutron diffraction measurements [139, 140, 145, 146] for niobium carbide. The data on short-range order in TiC_y, found by the magnetic susceptibility method [55, 89], agree fairly well with the results of studies of short-range order in titanium carbide by the method of diffuse neutron scattering [140, 145 – 147].

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References

1. Gusev A I, Rempel' A A *Nestekhiometriya, Besporyadok i Poryadok v Tverdom Tele* (Nonstoichiometry, Disorder, and Order in Solids) (Ekaterinburg: Izd. UrO RAN, 2001)
2. Gusev A I, Rempel A A, Magerl A J *Disorder and Order in Strongly Nonstoichiometric Compounds: Transition Metal Carbides, Nitrides, and Oxides* (Berlin: Springer-Verlag, 2001)
3. Gusev A I, Rempel A A *Phys. Status Solidi A* **163** 273 (1997)
4. Gusev A I *Usp. Fiz. Nauk* **170** 3 (2000) [*Phys. Usp.* **43** 1 (2000)]
5. Rempel' A A *Usp. Fiz. Nauk* **166** 33 (1996) [*Phys. Usp.* **39** 31 (1996)]
6. Nazarova S Z, Gusev A I *Zh. Strukt. Khim.* **42** 563 (2001) [*J. Struct. Chem.* **42** 470 (2001)]
7. Galoshina E V *Usp. Fiz. Nauk* **113** 105 (1974) [*Sov. Phys. Usp.* **17** 345 (1974)]
8. Kojima H, Tebble R S, Williams D E G *Proc. R. Soc. London Ser. A* **260** 237 (1961)
9. Kohlhaas R, Weiss W D *Z. Naturforsch. A* **20** 1227 (1965)
10. Stolyarov V V et al., in *Problemy Nanokristallicheskikh Materialov* (Advances in Nanocrystalline Materials) (Eds V V Ustinov, N I Noskova) (Ekaterinburg: Izd. UrO RAN, 2002) p. 409
11. Squire C F, Kaufmann A R *J. Chem. Phys.* **9** 673 (1941)
12. Taniguchi S, Tebble R S, Williams D E G *Proc. R. Soc. London Ser. A* **265** 502 (1962)
13. Kriessman C J *Rev. Mod. Phys.* **25** 122 (1953)
14. Kohlhaas R, Wunsch K M *Z. Angew. Phys.* **32** 158 (1971)
15. Suzuki H, Miyahara S *J. Phys. Soc. Jpn.* **20** 2102 (1965)
16. Hoare F E et al. *Proc. Phys. Soc. London Ser. B* **67** 728 (1954)
17. Wolcott N M *Philos. Mag.* **2** 1246 (1957)
18. Heiniger F, Bucher E, Muller J *Phys. Kondens. Mater.* **5** 243 (1966)
19. Collings E W, Ho J C *Phys. Rev. B* **2** 235 (1970)
20. Collings E W, Ho J C *Phys. Rev. B* **4** 349 (1971)
21. Heiniger F, Muller J *Phys. Rev.* **134** A1407 (1964)
22. Jensen M A, Maita J P *Phys. Rev.* **149** 409 (1966)
23. Kneip G D (Jr), Betterton J O (Jr), Scarbrough J O *Phys. Rev.* **130** 1687 (1963)
24. Betterton J O (Jr), Scarbrough J O *Phys. Rev.* **168** 715 (1968)
25. Corak W S et al. *Phys. Rev.* **102** 656 (1956)
26. Cheng C H et al. *Phys. Rev.* **126** 2030 (1962)
27. van der Hoeven B J C (Jr), Keesom P H *Phys. Rev.* **134** A1320 (1964)
28. Corsan J M, Cook A J *Phys. Lett. A* **28** 500 (1969)
29. Corsan J M, Cook A J *Phys. Status Solidi* **40** 657 (1970)
30. McMillan W L *Phys. Rev.* **167** 331 (1968)
31. Nazarova S Z, Gusev A I *Stekhiometricheskie Tverdye Rastvory Karbidov Niobiya i Tantala i Ikh Svoistva* (Stoichiometric Solid Solutions of Niobium and Tantalum Carbides and Their Properties) (Sverdlovsk: Ural'skii Nauchnyi Tsentr AN SSSR, 1987)
32. Shimizu M, Takahashi T, Katsuki A *J. Phys. Soc. Jpn.* **18** 1192 (1963)
33. Bakonyi I, Ebert H, Liechtenstein A I *Phys. Rev. B* **48** 7841 (1993)
34. Van Ostenburg D O et al. *J. Phys. Soc. Jpn.* **18** 1744 (1963)
35. Katsuki A, Shimizu M *J. Phys. Soc. Jpn.* **21** 279 (1966)
36. Costa P, Conte R R, in *Compounds of Interest in Nuclear Reactor Technology* (Spec. Rep., No. 13, Eds J T Waber, P Chiotti, W N Miner) (Edwards, Ann Arbor, Michigan: Inst. Metals Div., 1964) p. 3
37. Caudron R, Castaing J, Costa P *Solid State Commun.* **8** 621 (1970)
38. Marksteiner P et al. *Phys. Rev. B* **33** 812 (1986)
39. Okaz A M, Keesom P H *Phys. Rev. B* **12** 4917 (1975)
40. Schoen J M, Denker S P *Phys. Rev.* **184** 864 (1969)
41. Hörmandinger G et al. *Solid State Commun.* **68** 467 (1988)
42. Hobiger G et al. *J. Phys.: Condens. Matter* **2** 4595 (1990)
43. Barman S R, Sarma D D *Phys. Rev. B* **49** 16141 (1994)
44. Toth L E *Transition Metal Carbides and Nitrides* (New York: Academic Press, 1971) [Translated into Russian (Moscow: Mir, 1974)]
45. Marksteiner P et al. *Phys. Rev. B* **33** 6709 (1986)
46. Ishikawa M, Toth L E *Monatsh. Chem.* **103** 492 (1972)
47. Toth L E, Ishikawa M, Chang Y A *Acta Metall.* **16** 1183 (1968)
48. Gusev A I, Rempel A A *Phys. Status Solidi B* **151** 211 (1989)
49. Nazarova S Z, Kourov N I, Gusev A I *Zh. Fiz. Khim.* **62** 606 (1988)
50. Nemoshkalenko V V et al. *Metallofizika* **12** 3 (1990)
51. Ishikawa M, Toth L E *Phys. Rev. B* **3** 1856 (1971)
52. Selwood P W *Magnetochemistry* 2nd ed. (New York: Interscience Publ., 1956) [Translated into Russian (Moscow: IL, 1958)]
53. Vol'kenshtein N V, Galoshina E V, Shchegolikhina N I *Fiz. Met. Metalloved.* **25** 180 (1968)
54. Vol'kenshtein N V et al. *Zh. Eksp. Teor. Fiz.* **61** 1506 (1971) [*Sov. Phys. JETP* **34** 802 (1972)]
55. Zueva L V, Lipatnikov V N, Gusev A I *Zh. Fiz. Khim.* **73** 2163 (1999) [*Russ. J. Phys. Chem.* **73** 1952 (1999)]
56. Borukhovich A S et al. *Phys. Status Solidi* **36** 97 (1969)
57. Gusev A I, Zyryanova A N *Phys. Status Solidi A* **177** 419 (2000)
58. Borukhovich A S, Volkova N M *Izv. Akad. Nauk SSSR Neorg. Mater.* **7** 1529 (1971)
59. Borukhovich A S et al. *Fiz. Tverd. Tela* **11** 830 (1969)
60. Gusev A I, Rempel A A *Phys. Status Solidi A* **84** 527 (1984)
61. Lipatnikov V N et al. *Dokl. Akad Nauk SSSR* **297** 849 (1987) [*Sov. Phys. Dokl.* **32** 988 (1987)]
62. Ivanovskii A L et al. *Usp. Khim.* **52** 704 (1983)
63. Gubanov V A, Ivanovsky A L, Zhukov V P *Electronic Structure of Refractory Carbides and Nitrides* (Cambridge: Cambridge Univ. Press, 1994)
64. Redinger J et al. *J. Phys. Chem. Solids* **46** 383 (1985)
65. Bittner H, Goretzki H *Monatsh. Chem.* **93** 1000 (1962)
66. Lesnaya M I et al. *Izv. Akad. Nauk SSSR Neorg. Mater.* **13** 840 (1977)
67. Matveenko I I et al. *Izv. Akad. Nauk SSSR Neorg. Mater.* **1** 1062 (1965)
68. Genkin Ya E, Milovanova I A, Lyakutkin A V *Izv. Akad. Nauk Kaz. SSR Ser. Fiz.-Mat.* (2) 12 (1976)
69. Dubrovskaya L B, Matveenko I I *Fiz. Met. Metalloved.* **19** 199 (1965)
70. Santoro G *Trans. Met. Soc. AIME* **227** 1361 (1963)
71. Dubrovskaya L B, Nazarova S Z, Kachkovskaya E T *Izv. Akad. Nauk SSSR Neorg. Mater.* **20** 783 (1984) [*Inorg. Mater.* **20** (5) 674 (1985)]
72. Goretzki H "Untersuchung der magnetischen, elektrischen und thermoelektrischen Eigenschaften der Karbide und Nitride der 4a- und 5a-Übergangsmetalle", Ph.D. Thesis (Wien: Univ. Wien, 1963)
73. Valeeva A A, Rempel A A, Gusev A I *Neorg. Mater.* **37** 716 (2001) [*Inorg. Mater.* **37** 603 (2001)]
74. Valeeva A A, Rempel' A A, Gusev A I *Pis'ma Zh. Eksp. Teor. Fiz.* **71** 675 (2000) [*JETP Lett.* **71** 460 (2000)]
75. Takeuchi S, Suzuki K *J. Jpn. Inst. Metals* **33** 409 (1969)
76. Banus M D, Reed T B, Strauss A J *Phys. Rev. B* **5** 2775 (1972)
77. Aivazov M I, Gurov S V, Sarkisyan A G *Izv. Akad. Nauk SSSR Neorg. Mater.* **8** 213 (1972)
78. Ehrlich P *Z. Elektrochem.* **45** 362 (1939)
79. Denker S P *J. Appl. Phys.* **37** 142 (1966)
80. Vasil'ev Ya V, Khrychova D D, Ariya S M *Zh. Neorg. Khim.* **8** 788 (1963)
81. Takeuchi S, Suzuki K *J. Jpn. Inst. Metals* **33** 279 (1969)
82. Aivazov M I et al. *Izv. Akad. Nauk SSSR Neorg. Mater.* **7** 1180 (1971)
83. Valeeva A A, Rempel' A A, Gusev A I *Pis'ma Zh. Eksp. Teor. Fiz.* **73** 702 (2001) [*JETP Lett.* **73** 621 (2001)]
84. Gusev A I, Valeeva A A *Fiz. Tverd. Tela* **45** 1185 (2003) [*Phys. Solid State* **45** 1242 (2003)]
85. Mott N F *Metal-Insulator Transitions* (London: Taylor & Francis, 1974)
86. Rempel' A A, Gusev A I *Uporyadochenie v Nestekhiometricheskom Monocarbide Niobiya* (Ordering in Nonstoichiometric Niobium

Monocarbide) (Sverdlovsk: Ural'skii Nauchnyi Tsentr AN SSSR, 1983)

87. Rempel' A A et al. *Izv. Akad. Nauk SSSR Neorg. Mater.* **21** 596 (1985) [*Inorg. Mater.* **21** 514 (1985)]
88. Gusev A I, Rempel' A A *Fiz. Tverd. Tela* **27** 1528 (1985) [*Sov. Phys. Solid State* **27** 920 (1985)]
89. Zueva L V et al. *Dokl. Ross. Akad. Nauk* **365** 82 (1999) [*Dokl. Phys. Chem.* **365** 65 (1999)]
90. Zyryanova A N, Nazarova S Z, Gusev A I *Dokl. Ross. Akad. Nauk* **359** 348 (1998) [*Dokl. Phys. Chem.* **359** 91 (1998)]
91. Zyryanova A N, Gusev A I *Zh. Fiz. Khim.* **72** 2234 (1998) [*Russ. J. Phys. Chem.* **72** 2034 (1998)]
92. Gusev A I, Zyryanova A N *Pis'ma Zh. Eksp. Teor. Fiz.* **69** 296 (1999) [*JETP Lett.* **69** 324 (1999)]
93. Lipatnikov V N, Rempel' A A, Gusev A I *Zh. Neorg. Khim.* **33** 1860 (1988) [*Russ. J. Inorg. Chem.* **33** 1058 (1988)]
94. Gusev A I, Rempel A A, Lipatnikov V N *Phys. Status Solidi A* **106** 459 (1988)
95. Gusev A I, Rempel' A A *Fiz. Tverd. Tela* **26** 3622 (1984) [*Sov. Phys. Solid State* **26** 2178 (1984)]
96. Rempel' A A, Gusev A I *Kristallografiya* **30** 1112 (1985) [*Sov. Phys. Crystallogr.* **30** 648 (1985)]
97. Gusev A I, Rempel A A *Phys. Status Solidi A* **93** 71 (1986)
98. Landesman J P et al. *J. Phys. C: Solid State Phys.* **18** 809 (1985)
99. Lipatnikov V N et al. *J. Alloys Comp.* **261** 192 (1997)
100. Lipatnikov V N et al. *J. Phys.: Condens. Matter* **11** 163 (1999)
101. Gusev A I, Rempel A A, Lipatnikov V N *J. Phys.: Condens. Matter* **8** 8277 (1996)
102. Goretzki H *Phys. Status Solidi* **20** K141 (1967)
103. Karimov I et al. *Izv. Akad Nauk Uzb. SSR Ser. Fiz.-Mat. Nauk* (4) 81 (1979)
104. Lorenzelli N et al. *Solid State Commun.* **59** 765 (1986)
105. Lipatnikov V N et al. *Fiz. Tverd. Tela* **40** 1332 (1998) [*Phys. Solid State* **40** 1211 (1998)]
106. Dzhalabadze N V et al. *Fiz. Met. Metalloved.* **86** (1) 85 (1998) [*Phys. Met. Metallogr.* **86** 59 (1998)]
107. Lipatnikov V N, Gusev A I *Uporyadochenie v Karbidakh Titana i Vanadiya* (Ordering in Titanium and Vanadium Carbides) (Ekaterinburg: Izd. UrO RAN, 2000)
108. Gusev A I, Rempel' A A *Dokl. Ross. Akad. Nauk* **332** 717 (1993)
109. Lipatnikov V N et al., MSIT Workplace — Research Results No. 50.10097.9.20 (Stuttgart: MSI, 2002) p. 1
110. Gusev A I *Dokl. Akad. Nauk SSSR* **322** 918 (1992) [*Sov. Phys. Dokl.* **37** 84 (1992)]
111. Gusev A I, Rempel A A *J. Phys. Chem. Solids* **55** 299 (1994)
112. Rempel' A A et al., in *Ul'tradispersnye Poroshki, Nanostruktury, Materialy* (Ultradispersive Powders, Nanostructures, and Materials) (Krasnoyarsk: KGTU, 1999) p. 168
113. Rempel' A A et al. *Persp. Materialy* (6) 9 (1999)
114. Gusev A I et al. *Zh. Obshchei Khim.* **72** 1067 (2002) [*Russ. J. Gen. Chem.* **72** 997 (2002)]
115. Rempel' A A, Gusev A I *Pis'ma Zh. Eksp. Teor. Fiz.* **69** 436 (1999) [*JETP Lett.* **69** 472 (1999)]
116. Gusev A I, Rempel' A A *Nanokristallicheskie Materialy* (Nanocrystalline Materials) (Moscow: Fizmatlit, 2000)
117. Gusev A I, Rempel A A *Nanocrystalline Materials* (Cambridge: Cambridge Intern. Sci. Publ., 2004)
118. Volkova N M, Gel'd P V, in *Khimiya Soedinenii Redkikh Tugoplavkikh Elementov* (Chemistry of Compounds of Rare Refractory Elements) [Tr. Inst. Khimii UF AN SSSR (Proc. of the Inst. of Chemistry of the Urals Branch of the USSR Acad. of Sci.] No. 14 (Sverdlovsk: Inst. Khimii UF AN SSSR, 1967) p. 41
119. Emmons G H, Williams W S *J. Mater. Sci.* **18** 2589 (1983)
120. Athanassiadis T, Lorenzelli N, de Novion C H *Ann. Chim.* (Paris) **12** 129 (1987)
121. Lipatnikov V N et al. *Fiz. Tverd. Tela* **41** 529 (1999) [*Phys. Solid State* **41** 474 (1999)]
122. Gusev A I *Zh. Fiz. Khim.* **74** 600 (2000) [*Russ. J. Phys. Chem.* **74** 510 (2000)]
123. Yasui M, Shimizu M *J. Phys. F: Metal Phys.* **15** 2365 (1985)
124. Gusev A I *Fizicheskaya Khimiya Nestekhiometricheskikh Tugoplavkikh Soedinenii* (Physical Chemistry of Nonstoichiometric Refractory Compounds) (Moscow: Nauka, 1991)
125. Vonsovskii S V *Magnetizm* (Magnetism) (Moscow: Nauka, 1971) [Translated into English in 2 Vols (New York: J. Wiley, 1974)]
126. Dubrovskaya L B, Rabin'kin A G, Gel'd P V *Zh. Eksp. Teor. Fiz.* **62** 300 (1972) [*Sov. Phys. JETP* **35** 161 (1972)]
127. Geld P V et al. *Phys. Status Solidi B* **42** 85 (1970)
128. Redinger J et al. *J. Phys. Chem. Solids* **47** 387 (1986)
129. Rempel' A A et al. *Fiz. Tverd. Tela* **28** 279 (1986) [*Sov. Phys. Solid State* **28** 153 (1986)]
130. Rempel' A A et al. *Zh. Fiz. Khim.* **61** 1761 (1987) [*Russ. J. Phys. Chem.* **61** 919 (1987)]
131. Rempel' A A, Gusev A I *Fiz. Tverd. Tela* **32** 16 (1990) [*Sov. Phys. Solid State* **32** 8 (1990)]
132. Rempel A A, Gusev A I *Phys. Status Solidi B* **160** 389 (1990)
133. Rempel' A A *Effekty Uporyadocheniya v Nestekhiometricheskikh Soedineniyakh Vnedreniya* (Ordering Effects in Nonstoichiometric Interstitial Compounds) (Ekaterinburg: Nauka, 1992)
134. Gusev A I, Rempel' A A *Strukturnye Fazovye Perekhody v Nestekhiometricheskikh Soedineniyakh* (Structural Phase Transitions in Nonstoichiometric Compounds) (Moscow: Nauka, 1988)
135. Gusev A I, Rempel A A, in *Materials Science of Carbides, Nitrides and Borides* (Eds Y G Gogotsi, R A Andrievski) (Dordrecht: Kluwer Acad. Publ., 1999) p. 47
136. Billingham J, Bell P S, Lewis M H *Acta Crystallogr. A* **28** 602 (1972)
137. Sauvage M, Parthé E *Acta Crystallogr. A* **28** 607 (1972)
138. Sauvage M, Parthé E, Yelon W B *Acta Crystallogr. A* **30** 597 (1974)
139. De Novion C H, Maurice V *J. Phys. Colloq.* (Paris) **38** C7-211 (1977)
140. Moisy-Maurice V et al. *Solid State Commun.* **39** 661 (1981)
141. Hiraga K, Hirabayashi M *J. Phys. Colloq.* (Paris) **38** C7-224 (1977)
142. Gusev A I *Phys. Status Solidi B* **156** 11 (1989)
143. Froidevaux C, Rossier D *J. Phys. Chem. Solids* **28** 1197 (1967)
144. Rempel A A, Gusev A I, Belyaev M Yu *J. Phys. C: Solid State Phys.* **20** 5655 (1987)
145. Priem T et al. *Physica B* **156–157** 47 (1989)
146. Moisy-Maurice V "Structure atomique des carbures non-stoechiometriques de metaux de transition", Rapport CEA-R-5127 (Gif-sur-Yvette (France): Commissariat a l'Energie Atomique, 1981)
147. De Novion C H et al., in *The Physics and Chemistry of Carbides, Nitrides and Borides* (Ed. R Freer) (Dordrecht: Kluwer Acad. Publ., 1990) p. 329