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Short-range Order and Local Displacements of the Atoms in Non-stoichiometric Compounds

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Published data on the local distribution of the atoms and their displacements in non-stoichiometric transition metal carbides and nitrides have been reviewed. The phenomena of short-range order in disordered and ordered non-stoichiometric compounds, and their solid solutions, have been discussed in detail. Data on the static displacements of the atoms in disordered carbides and nitrides have been analysed. The possibilities for the further study of the distribution of the atoms in non-stoichiometric compounds have been discussed.
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I. INTRODUCTION

In recent years there has been a continuous increase in interest in the study of the structures of transition metal carbides and nitrides. This is due chiefly to the use of highly sensitive experimental methods, which have established that the distribution of non-metal atoms in these compounds is not statistical, as previously assumed. Another reason for the interest in non-stoichiometric carbides and nitrides is related to their properties. These compounds are among the most refractory materials; the melting points T_f of most of them exceed 3500 K, and tantalum carbide has the highest known melting point, T_f = 4270 K; they are radiation-stable superconductors with transition temperatures to the superconducting state $\leqslant$17 K. In addition, they are extremely hard, their hardness approaching that of diamond. Another characteristic of non-stoichiometric compounds is the possible formation of unrestricted reciprocal solid solutions, so that their physicochemical characteristics can be influenced considerably by replacing the metal and non-metal atoms. The properties of non-stoichiometric compounds are directly related to their structural state, that is to the presence or absence of correlations and short-range or long-range order in the relative positions of the atoms.

In the present work, an attempt has been made to systematise the comparatively few but nevertheless important data obtained in the last 10–15 years in the study of the local distribution of the atoms and their displacements in non-stoichiometric compounds and their solid solutions. Before discussing these results, however, it is appropriate to give a general description and examination of the principal characteristics of the crystal structure and the chemical bonding in non-stoichiometric compounds of the transition metals, necessary for the subsequent discussion.

Non-stoichiometric compounds are often called interstitial phases, indicating that a characteristic of their structure is the presence of a face-centred cubic (FCC) or hexagonal close-packed (HCP) metal lattice with interstitial non-metal atoms in the octahedral interstices. At the same time, the symmetry of the metal lattice in the carbides and nitrides differs from that of the crystal lattice of the corresponding transition metals, that is the crystal structure of the metal changes on formation of the carbides and nitrides (cobalt is an exception). The group IV transition metals (titanium, zirconium, hafnium), which have an HCP structure, form carbides and nitrides with an FCC metal sub-lattice. Transition metals with a body-centred structure (vanadium, niobium, tantalum, chromium, molybdenum, tungsten) form carbides and nitrides with FCC or HCP metal sub-lattices. The change in the crystal structure of the metal on formation of the carbide or nitride indicates fairly strong interactions between the metal and non-metal atoms, so that the application of the term "interstitial phase" to these substances is not completely justified. In the narrow sense of the word, only restricted interstitial solid solutions are true interstitial phases.

The concept of "interstitial phase" (or "interstitial alloy") has recently been used fairly widely. It is used to describe a wide range of phases with related structures, formed as a result of the insertion of hydrogen, nitrogen, carbon, oxygen, boron, or silicon atoms into the interstices in the crystal lattice of a transition metal. Both interstitial solid solutions and the transition metal hydrides, carbides, nitrides, oxides, and borides, and also the reciprocal substitutional solid solutions formed by these compounds, are interstitial phases. These compounds are also called compounds of variable composition, emphasising the existence of wide homogeneity ranges, within which the composition of the compound may deviate considerably from the stoichiometric composition with preservation of the crystal structure. Since the deviation from stoichiometry, that is non-stoichiometry, is a characteristic property of these compounds, it is more correct to call them non-stoichiometric compounds of the interstitial phase type. This term emphasises that these substances (carbides, nitrides, etc.) are compounds, and not interstitial solid solutions, and at the same time draws attention to the most important characteristics of their structure, namely the location of the non-metal atoms in the interstices of the metal sub-lattice and the possibility that the composition deviates considerably from the stoichiometric.

In the full sense of the term, only the carbides, nitrides, and lower oxides of the transition metals can be described as non-stoichiometric compounds of the interstitial phase type. Thus the stability of the hydrides and the limiting concentration of hydrogen in them may change with change in the external conditions. The difference between transition metal hydrides and solid solutions of hydrogen in transition metals therefore becomes indistinct. The borides and

more particularly the silicides have practically no homogeneity ranges; moreover, in these materials a fairly important role is played by direct B—B and Si—Si bonds (in the carbides, nitrides, and oxides, direct interactions between the non-metal atoms are negligible). The higher oxides also have practically no homogeneity ranges. In the present review, therefore, the carbides, nitrides, and lower oxides of the transition metals are regarded as non-stoichiometric compounds of the interstitial phase type.

A characteristic feature of non-stoichiometric compounds is the, as it were, independent existence of the sub-lattice of the pure metal, which acts as the matrix for the atoms which are introduced into its interstices and which form the non-metal sub-lattice. The pure metals can be regarded as a unique type of interstitial phase corresponding to unoccupied interstices, and the unoccupied interstices can be regarded as "holes", equivalent to interstitial atoms. When the non-metal sub-lattice is partly occupied, the unoccupied interstices (structural vacancies) can diffuse through the lattice and behave like real interstitial atoms. Thus the structural vacancies in non-stoichiometric compounds of the interstitial phase type can be regarded in a first approximation as analogues of interstitial atoms.[1-4] Thus deviation from stoichiometry can be (and is) examined using the theory of substitutional solutions, whose components are interstitial atoms and structural vacancies. The deviation from stoichiometry leads to a change in all the properties of non-stoichiometric compounds.[3-9] The defect character of the crystal structure, that is the presence of a high concentration of structural vacancies, is apparently one of the most important characteristics of non-stoichiometric compounds.

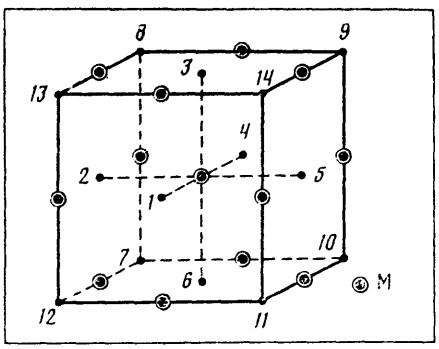


Figure 1. NaCl structure and the immediate environment of the metal atom: (1—6) first coordination sphere, formed by six sites of the non-metal sub-lattice; (7—14) second coordination sphere, formed by eight sites of the non-metal sub-lattice; twelve metal atoms form an independent coordination sphere (M represents a metal atom; the sites of the non-metal sub-lattice are numbered).

Non-stoichiometric transition metal monocarbides, mononitrides, and monoxides MX have the NaCl structure. In this structure (Fig.1), the non-metal atoms occupy statistically the octahedral interstices of the metal sub-lattice, so that each metal atom is in an octahedral environment of six sites of the non-metal sub-lattice, which form the first non-metal coordination sphere; the second non-metal coordination sphere is formed by eight sites of the non-metal sub-lattice; twelve metal atoms form an independent metal coordination sphere, situated between the first and second non-metal coordination spheres. The lower carbides and nitrides with the composition M_2X have the hexagonal $W_2C(L'3)$ structure, in which the non-metal atoms occupy statistically half of the octahedral interstices.

An analysis of theoretical considerations[10-15] and a large number of calculations by zone and cluster methods led to the formulation[8,16] of the principal regular features of the structure of the valence zone of non-stoichiometric compounds with the NaCl structure. According to Refs.8 and 16, the valence zone of these compounds includes a low-energy $2s$(X) band containing small contributions from the s-, p-, and d-states of the metal; the principal valence-bonding band, formed by strong mixing of the $2p$(X) and d(M) functions; and a high-energy partly occupied conductivity band, formed chiefly by nd(M) functions with a small contribution from $2p$(X), $(n+1)p$(M), and $(n+1)s$(M) functions. The redistribution of the individual atomic states on the formation of non-stoichiometric compounds leads to partial charge transfer between the metal and non-metal atoms, and this is responsible for the ionic component of the chemical bond.

Thus in non-stoichiometric compounds there is a combined covalent—metallic—ionic chemical bond.[8,16] With increase in the concentration of vacancies, the populations of the single bonds M—X increase, but the number of such bonds decreases with a simultaneous decrease in the charge localised on the atoms; this leads to a decrease in the ionic component of the bond. In addition, the deviation from stoichiometry is accompanied by an increase in the width and population of the d-band of the metal and a decrease in the width of the $2p$(X) band, and this can be regarded as an increase in the strength of the M—M interactions and a decrease in the covalent component of the M—X bond.

More detailed information on non-stoichiometric compounds can be found in a number of monographs.[1,3-8]

II. SHORT-RANGE ORDER IN NON-STOICHIOMETRIC COMPOUNDS

The presence of structural vacancies and the possibility of their redistribution within the lattice, together with the combined type of chemical bond, are responsible for the fairly wide occurrence in non-stoichiometric compounds of correlations and of short-range or long-range order in the relative arrangement of the atoms.

Any disorder destroys the crystal symmetry and leads to a decrease in the degree of long-range order. The simplest type of disorder occurs in ideal binary substitutional solid solutions. In an ideal solid solution, when an atom A is replaced by an atom B, the crystal lattice is not distorted, and the sites in which this replacement has taken place are distributed randomly, that is statistically, in space. In this case the probability of finding an atom of a given element in any site of the crystal lattice is equal to the atomic fraction of this element in the solid solution. Thus in an ideal solution, the occupancy of a given site by an atom of a given element is independent of the nature of the occupancy of the other sites, both neighbouring and distant. In a real crystal, the atoms of different elements have different masses and dimensions, so that the energies of interaction between atoms of the same kind and atoms of different kinds differ considerably. It is for this reason that statistical

disorder in a crystalline solid can arise only at sufficiently high temperatures, when the forces of interatomic interaction are small compared with the energy of the thermal vibrations. This state can be "frozen" by quenching, that is by cooling rapidly to low temperatures, at which the diffusion mobility of the atoms is negligible.

In non-stoichiometric compounds, statistical distribution of the interstitial atoms and structural vacancies is also obtained by rapid cooling. For a long time it was assumed that for non-stoichiometric compounds this disordered state was the only one possible, and it is only in recent decades that it has become clear that this is not the case. It has been found that on comparatively slow cooling of non-stoichiometric compounds, the statistical distribution gives way to correlations in the arrangement of the atoms and vacancies in neighbouring lattice sites, as a result of which the atoms of a given element may be surrounded preferentially by atoms of the same or another element (or vacancies), that is short-range order may be observed.

The arrangement of the atoms in the crystal lattice of non-stoichiometric compounds can be characterised by the long-range and short-range order. In the present review, particular attention is paid to recent studies of short-range order and the associated local displacements of the atoms in refractory non-stoichiometric compounds and their solid solutions.

The principal experimental methods for studying short-range order in non-stoichiometric compounds of the interstitial phase type are nuclear magnetic resonance (NMR) and the diffuse scattering of neutrons (to study the distribution of interstitial atoms) and X-rays (to study the distribution of metal atoms). None of these methods is universal (applicable to all non-stoichiometric compounds) in giving information on the nature of the distribution of the atoms of all elements. NMR has the most restricted range of applicability, since magnetic resonance signals are given only by nuclei with a non-zero spin I, which have a magnetic moment. Thus NMR studies are possible in principle for non-stoichiometric compounds of vanadium, niobium, and tantalum, since the most abundant isotopes of these metals have nuclei with $I \neq 0$. On the other hand, NMR cannot be used to study the non-stoichiometric compounds of the group IV transition metals (titanium, zirconium, hafnium), since the nuclei of the most abundant isotopes of these metals do not have a magnetic moment.

As far as the interstitial atoms (carbon, nitrogen, oxygen) are concerned, the nuclei of the abundant isotopes ^{12}C and ^{16}O have zero spin, and magnetic resonance cannot be observed. The most abundant nitrogen isotope ^{14}N has a magnetic moment ($I = 1$), but no ^{14}N NMR studies of non-stoichiometric compounds of the interstitial phase type have yet been carried out. The NMR study of the nuclei of the carbon isotope ^{13}C with spin 1/2, which would increase considerably the amount of information on the nature and structure of non-stoichiometric carbides, appears extremely promising.

In those cases where it is possible in principle, the use of NMR to study non-stoichiometric compounds is extremely effective, because of the high sensitivity of the method to slight changes in the symmetry of the environment of the resonating atoms.

1. NMR Studies of Short-range Order

NMR can be used to determine the relative positions of interstitial atoms and structural vacancies in the non-metal sub-lattice of non-stoichiometric compounds, that is to study the nature of the short-range order in them. In addition, NMR reveals various characteristics of the electronic structure of non-stoichiometric compounds.

A special notation will be used for convenience in the subsequent discussion. The immediate environment of a metal atom in a carbide MC_y or a nitride MN_y with the NaCl($B1$) structure includes two coordination spheres formed by sites of the non-metal sub-lattice, and one coordination sphere formed by metal atoms (see Fig.1). It is convenient to denote the position of a metal atom in this environment by means of subscripts and superscripts giving the numbers of vacancies in the first and second coordination spheres respectively, formed by the sites of the non-metal sub-lattice; for example, the metal atom position M_0^2 indicates that its first coordination sphere is complete (contains no vacancies), while the second coordination sphere contains two vacancies.

Among the non-stoichiometric compounds, the vanadium compounds have been studied in most detail. VC_y specimens with $y = 0.66$, 0.7, 0.8, 0.84, and up to $y = 0.87$, that is throughout the homogeneity range of vanadium carbide, have been studied.[17] The ^{51}V NMR spectra of the carbides $VC_{0.875}$, $VC_{0.84}$, and $VC_{0.70}$ showed several resonance lines, whose intensity changed with change in the composition of VC_y. Comparison of the total intensity of the resonance lines in metallic vanadium and its carbides showed that NMR makes it possible to detect practically all the vanadium nuclei in VC_y, irrespective of its composition. At the same time, the presence of vacancies in the carbon sub-lattice of VC_y had a significant influence on the relative intensity of the observed resonance lines. The lines and their satellites in the ^{51}V NMR spectra were associated with the positions of vanadium atoms in VC_y having definite configurations of the vacancies in the first coordination sphere.[17] This identification was possible since the electric field gradient of vanadium nuclei with no vacancies in the first coordination sphere should be much smaller than that for vanadium nuclei having one or several vacancies. Thus the observed lines were associated with the positions of vanadium atoms V_0 (without vacancies in the first coordination sphere), V_1, V_2, and V_3 (with one, two, and three vacancies respectively in the first coordination sphere).

A relationship was also established[17] between the number of vacancies n in the immediate environment of a vanadium atom and the sharp change in the Knight shift (K):

$$K_n - K_{n-1} \approx nK_0, \qquad (1)$$

where $K_0 \simeq 0.07-0.09\%$, that is the change in K is proportional to the number of vacancies in the first coordination sphere of a vanadium atom in VC_y.

In Ref.17, to investigate the nature of the distribution of the vacancies in vanadium carbide, the experimentally determined probability distribution $P(n)$ of the positions of the vanadium atoms n was compared with the random probability distribution, calculated from the equation:

$$P(n) = C_6^n (1-y)^n y^{6-n}. \qquad (2)$$

The experimental distribution differed from the random distribution for all VC_y specimens studied; for example, the probability of the position V_0 decreases much more rapidly than for the random distribution, and the V_3 positions are encountered much less frequently than in the statistical distribution. The small number of V_3

positions and the absence of vanadium atom positions with more than three vacancies in the first coordination sphere were attributed to repulsion between neighbouring vacancies. Thus the existence of short-range order in a non-stoichiometric compound, namely vanadium carbide, was established experimentally for the first time.[17]

In the same work,[17] NMR was used for the first time to study the ordered phase of a non-stoichiometric compound. The ^{51}V NMR spectrum of $VC_{0.875}$ differed considerably from the spectra of vanadium carbide specimens with other compositions. In particular, the ratio of the intensities of the lines corresponding to the positions V_0 and V_1 was 1/3. If the relative intensity of each line is proportional to the relative number of corresponding positions, this intensity ratio can be explained if in the carbide $VC_{0.875}$ three quarters of all the vanadium atoms have one vacancy in the first coordination sphere, and the others have a complete environment. This distribution of the vacancies indicates the existence of a superstructure of the V_8C_7 type with space group $P4_332$ or $P4_132$. It should be noted, however, that in the opinion of the authors cited,[17] this model of the distribution of the vacancies does not provide a completely accurate description of the real lattice. Thus this superstructure with helical arrangement of the vacancies contains only the positions V_0^1 and V_1^1, whereas study of the satellites indicates the existence of three types of position V_1, which could not be distinguished by the authors cited.[17] Moreover, the proposed distribution of the atoms in the ordered carbide V_8C_7 cannot be described by the space group $P4_332$.

Interesting results revealing another ordered structure were obtained in an NMR study of an annealed single crystal of vanadium carbide $VC_{0.84}$.[18,19] The ^{51}V NMR spectra obtained were broken down into lines corresponding to the positions V_0 and V_1. An analysis of the satellites made it possible to break down the intense line V_1 into lines corresponding to the positions V_1^0, V_1^1, and V_1^2 (without vacancies and with one and two vacancies in the second coordination sphere). The ratio of the intensities of the V_1^1 and V_1^2 lines in the spectra was 2:1, so that in the carbide studied, the number of V_1^1 positions is apparently twice the number of V_1^2 positions. The higher intensity of the lines corresponding to the V_1^1 and V_1^2 positions makes it possible to regard them as the positions of the ordered structure of vanadium carbide. In an electron diffraction study of $VC_{0.84}$,[18] the trigonal symmetry of the ordered vanadium carbide V_6C_5 was proposed; the use of the NMR data on the ratio of the numbers of the positions V_1^1 and V_1^2 made it possible to describe the distribution of the carbon atoms and the vacancies in the trigonal unit cell, that is to determine the structure of V_6C_5. The presence of weak lines corresponding to the positions V_0 and V_1^0 was attributed to the deviation of the composition of the carbide studied from the composition of the ordered phase $VC_{0.83}$ (that is V_6C_5). The presence of these lines in the spectrum may also be related to the deviation of the degree of long-range order in the specimens studied from the maximum possible.

These NMR studies [17–19] gave a qualitative picture of the distribution of the carbon atoms and vacancies in the non-metal sub-lattice of vanadium carbide. The next step was an attempt to obtain quantitative information on the short-range order in VC_y by minimising the ^{51}V NMR spectra.[20,21] The experimental ^{51}V NMR spectra obtained[20] for $VC_{0.75}$, $VC_{0.84}$, $VC_{0.85}$, $VC_{0.86}$, and $VC_{0.87}$ are analogous to the spectra previously described[17] and contain resonance lines corresponding to the positions V_0, V_1, and V_2. Assuming that the complex form of the line in the spectrum is due to the presence in the crystal of nuclei with different local environments, and that the intensity of a signal is proportional to the number of positions of a given type, the following relationship was obtained for calculating the intensity

$$I_p(\nu) = \sum_i \lambda_i P_i I_i(\nu), \qquad (3)$$

where P_i is the probability of the cluster with the i-th configuration of the immediate environment of non-metal atoms round the resonating nucleus (for non-stoichiometric compounds with the NaCl structure, an octahedron of six sites of the non-metal sub-lattice with a metal atom at its centre is taken as the basis cluster figure); λ_i the multiplicity of the i-th configuration of the octahedral cluster; and $I_i(\nu)$ a mathematical model of the ideal spectral line, corresponding to the i-th configuration of the immediate environment of the resonating nucleus (in Ref.20 the lines were described by a Gaussian distribution). The probabilities P_i were expressed by expansion with respect to paired and many-particle correlation parameters by the published method.[22]

The minimisation of the ^{51}V NMR spectra for VC_y with successive allowance for the correlation parameters, beginning with the paired parameters and ending with the sixth-order correlation parameters, showed[20,21] that the best description of the spectrum is achieved by taking account of paired and three-fold correlations. Allowance for correlations of higher orders did not lead to any significant change in the calculated spectrum. According to the results obtained, the paired correlations ε_{21} describing the nature of the distribution of the carbon atoms (or vacancies) in two neighbouring sites of the octahedron situated relative to one another in the first coordination sphere are negative throughout the homogeneity range of vanadium carbide. This means that throughout the homogeneity range of VC_y, the probability of detecting neighbouring vacancies is smaller than that for the statistical distribution. The short-range parameter for the first coordination sphere $a_1 = \varepsilon_{21}/y(1-y)$ is approximately –0.1, increases slowly with the increase in the deviation from stoichiometry, and shows a slight minimum close to the composition $VC_{0.83}$.

Thus the results of the calculation of the correlations and the short-range order parameter in vanadium carbide on the whole agree with the conclusions[17–19] that in VC_y there is short-range order due to the repulsion of vacancies. At the same time, it was incorrectly stated in Ref.21 that the production of the ordered phases of vanadium carbide is due to the existence of a definite type of short-range order. As shown in Refs.23–27, in non-stoichiometric compounds with the NaCl structure, long-range order may not be produced even when there is maximum short-range order in the first and second coordination spheres, so that the existence of short-range order in these compounds is only a necessary but not a sufficient condition for the production of long-range order.

The influence of composition on the ^{51}V NMR spectra of the compounds VN_y ($0.980 \leqslant y \leqslant 0.706$) has been studied.[28] The total intensity of the NMR signal, normalised for the quantity of vanadium, was found to be constant for all values of y. This means that, as in the case of VC_y, in the nitrides VN_y studied all the vanadium nuclei contribute to the resonance absorption line, so that quantitative analysis of the results is possible. The resonance peak observed in the spectra was broken down into two lines, corresponding to the complete position V_0 and the positions of vanadium atoms with one or more vacancies in the first coordination sphere. At a high concentration of vacancies, a systematic deviation of the experimentally observed intensity of the resonance lines from the intensity calculated in the approximation of a random distribution of the nitrogen atoms and vacancies was observed. This indicates that

the nitrogen atoms and vacancies are distributed with a certain degree of order in the non-metal sub-lattice of vanadium nitride.

A quantitative analysis of the short-range order in vanadium nitride was carried out[21] using the same scheme as for vanadium carbide. Minimisation of the NMR spectra established a regular change in the paired and three-fold correlation parameters with change in the composition of the nitride VN_y. According to the calculation, throughout the homogeneity range of VN_y, the parameter ε_{21} is negative and decreases, and the parameter ε_{22} is positive and increases, with increase in the number of vacancies. This means that in vanadium nitride there is short-range order with preferential arrangement of the vacancies at opposite vertices of the octahedron, whose six sites form the first coordination sphere of the vanadium atom.

Cubic vanadium monoxide VO_y has been studied by spin echo and broad-line NMR methods in the temperature range 1.4 to 300 K.[29,30] The ^{51}V NMR spectra showed only one line, whose width increased with increase in the oxygen concentration in VO_y. The measurements also showed that the magnitude of the Knight shift is independent of temperature and the composition of VO_y.

NMR has been used to study short-range order not only in non-stoichiometric compounds of vanadium, but also in solid solutions, chiefly vanadium oxide carbides and oxide nitrides.[21,31] The ^{51}V NMR spectra of the oxide carbides VC_xO_y consist of sets of four lines, whose widths and positions are practically independent of the composition of the oxide carbide. From a comparison of the integral intensity of the ^{51}V NMR spectra of the carbide $VC_{0.87}$ and the oxide carbide VC_xO_y ($x + y = 0.75-0.94$), it was concluded[21] that all the vanadium nuclei contribute to the spectrum of the oxide carbide; in the oxide carbides rich in oxygen ($y \geqslant 0.4$), vacancies are present not only in the non-metal sub-lattice but also in the metal sub-lattice, but no influence of the vacancies in the metal sub-lattice on the integral intensity of the NMR spectra could be detected.

In the analysis of the NMR spectra, the observed lines were associated with non-equivalent positions of the vanadium atoms; it was noted that the intensity of the lines is determined by the concentration of oxygen in the specimens studied. According to Ref.21, all the lines correspond to a complete environment of C and O atoms simultaneously round the vanadium atoms, but the ratio of the numbers of C and O atoms may be different, for example $[VC_5O_1]$, $[VC_4O_2]$, $[VC_1O_5]$, $[VC_3O_3]$. The intensities of the lines in the spectrum are determined by the probabilities of the corresponding positions. Comparison of the experimentally determined values of the probabilities with the values calculated assuming a statistical distribution of the C and O atoms showed that the distribution of the non-metal atoms is close to random for $V_{0.61}O_{0.14}$ and $VC_{0.67}O_{0.15}$, and differs considerably from the random distrubtion at high oxygen concentrations.

In the ^{51}V NMR spectra of the oxide nitrides VN_xO_y, the authors cited[21] observed three lines, two of which, by analogy with VC_xO_y, were associated with the positions $[VN_5O_1]$ and $[VN_3O_3]$.

An analysis of the ^{51}V NMR spectra of solid solutions VC_xO_y, VN_xO_y, and VC_xN_y [21] established that the replacement of one of the atoms forming the immediate environment of a vanadium atom by an atom of another element leads to an increase in the Knight shift compared with that for a uniform complete environment. The highest value of the Knight shift is observed for equal numbers of the atoms of the two elements in the first coordination sphere of the vanadium atom. It may be noted that in vanadium carbide, nitride, and oxide, the Knight shift also increases with increase in the number of vacancies in the immediate environment of the vanadium atom.

Taken together, these data indicate that the introduction of any impurity defect into the immediate environment of the metal atom in a non-stoichiometric compound should lead to an increase in the Knight shift compared with that for a uniform complete environment (the particles whose relative fraction in the first coordination sphere of the metal atom is smaller are regarded as the impurity defect).

Only a few papers have been devoted to the ^{93}Nb NMR study of non-stoichiometric compounds of niobium. Here, mention may be made of Ref.32, where NMR was used for the phase analysis of niobium nitride NbN_7. According to the results obtained, the phases correspond to definite lines in the NMR spectrum, and it is possible to establish from the spectrum which phases are present in the specimen being studied. It was also noted[32] that the quadrupole interactions in niobium nitride are stronger than those in vanadium nitride.

In the ^{93}Nb NMR spectra of NbC_y specimens,[17] only one line was detected, whose intensity decreased rapidly on going from $NbC_{0.94}$ to $NbC_{0.90}$; the intensity of this line decreased only slightly with further decrease in the carbon concentration. This line was assigned to the positions of niobium atoms having a complete environment as far as the third coordination sphere.

The short-range order in NbC_y has been studied in detail by highly sensitive pulse NMR spectroscopy.[23,33-36] Specimens of non-stoichiometric niobium carbide NbC_y ($0.995 \leqslant y \leqslant 0.75$) were obtained by sintering niobium and carbon powders. To obtain niobium carbide specimens in states with different degrees of order, the specimens synthesised were subjected to thermal treatment under different conditions of temperature, heating time, and rate of cooling. The conditions of the thermal treatment had a significant influence on the phase composition of the specimens; heating at temperatures above the temperature of the order–disorder transition (1304 K for $NbC_{0.83}$ [23]) with subsequent quenching (conditions *a*) gave niobium carbide specimens in the disordered state. Heating at 1300 K with subsequent slow cooling (conditions *c*) led to the formation of an ordered phase. Heating at 1300 K with rapid cooling (conditions *b*) gave specimens containing ordered and disordered phases simultaneously. The conditions of thermal treatment will subsequently be indicated after the niobium carbide composition, for example $NbC_{0.88}(c)$.

The ^{93}Nb NMR spectra of the carbides NbC_y, obtained[23,33,34] on a Bruker SXP4-100 pulse spectrometer at frequencies of 22.0, 21.5, and 14.01 MHz, are shown in Figs.2 and 3. Most of the spectra contain a line *O*, whose position coincides with that of the line observed[17] in the NMR spectra of niobium carbide. With increase in the defect character of the carbon sub-lattice, this line becomes less intense and then disappears; in spectrum IV, however, corresponding to $NbC_{0.75}(b)$, the line *O* appears again (Fig.2). The slower decrease in the intensity of the line *O*, compared with the data in Ref.17, on going from $NbC_{0.995}$ to $NbC_{0.845}$, and the increase in its width, do not make it possible to assign this line to positions of niobium atoms with a complete environment up to the third coordination sphere, as was done in Ref.17. It is logical to assume that the line *O* in spectra *I*–*IV* (Fig.2) corresponds both to complete positions Nb_0^0 (Fig.4*a*) and to niobium atom positions containing vacancies only in the third coordination sphere, for example Nb_0^1 (Fig.4*b*), Nb_0^2, etc.

Fig.3, which shows the change in the form of the spectra with change in the degree of order, gives the ^{93}Nb NMR spectra obtained at frequencies of 21.5 MHz and 14.01 MHz for specimens with the composition $NbC_{0.83}$, subjected to thermal treatment under the three

conditions. Spectrum *I* for the specimen $NbC_{0.83}(a)$ contains one broad peak on either side of the line *O*; spectra *II* and *III* for the specimens $NbC_{0.83}(b)$ and $NbC_{0.83}(c)$ contain five peaks in addition to the line *O*. Spectra *IV* and *V* were obtained for the same specimens as spectra *I* and *II*, but at a lower frequency (Fig.3). The low relative intensity (~4%) of the line *O* (spectrum *II* in Fig.3), assigned to the positions Nb_0, and the approximately equal numbers of positions Nb_0 and Nb_2 in $NbC_{0.83}$ indicate that the peaks observed in spectrum *II* are associated chiefly with the positions Nb_1 (the peaks corresponding to the positions Nb_2 are not observed, in accordance with the second-order quadrupole effect).

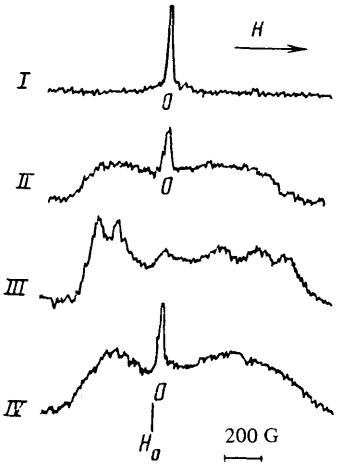


Figure 2. Change in the form of the ^{93}Nb NMR spectra with change in the composition of niobium carbide NbC_y (ν_0 = 21.5 MHz, H_0 = 20.69 kG); (*I*) $NbC_{0.995}$, (*II*) $NbC_{0.88}$ (*b*), (*III*) $NbC_{0.845}(b)$, (*IV*) $NbC_{0.75}(b)$.[34]

An analysis[33,34] of the frequency dependence of the positions of the peaks in the NMR spectra (spectra *II* and *V* in Fig.3) shows that the satellites can be only *O'* peaks, and the line of the central transition for them is the line *O*. The positions of the remaining peaks change with change in frequency, so that they are not satellites, but central transition lines. The broadening of the NMR spectra at low frequencies indicates that the contribution of quadrupole interactions is greater than that of the magnetic, so that the positions of the peaks *A*, *B*, *A'*, *B'* (spectrum *II*) and *A*, *B*, *A'*, *B'*, *C'*, *D'* (spectrum *V*) coincide with the positions of unique points of split central transition lines (the satellites of these lines are not observed, in accordance with the first-order quadrupole effect).

As a consequence of the asymmetry and high values of the electric field gradient, the positions of the peaks in the NMR spectra obtained at different frequencies change in a fairly complex fashion, so that in Refs.23, 33, and 34 a calculation was carried out making it possible to distinguish in spectra *II*, *III*, and *V* (Fig.3) the peaks assigned to different lines of the central transition. The calculation showed that in the NMR spectra of the carbide $NbC_{0.83}$ (Fig.3), in addition to the line *O*, it is possible to distinguish another four central transition lines. The positions of the unique points of the central transition lines and the corresponding parameters of the hyperfine interactions (the frequency of the quadrupole coupling ν_Q, the electric field gradient asymmetry parameter η_{as}, and the Knight shift *K*) are given in Table 1.

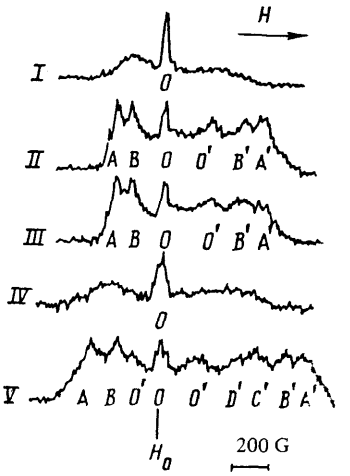


Figure 3. Influence of ordering on the ^{93}Nb NMR spectra of the carbide $NbC_{0.83}$; (*I*, *IV*) conditions *a*; (*II*, *V*) conditions *b*; (*III*) conditions *c* (*I*–*III*—ν_0 = 21.5 MHz, H_0 = 20.69 kG; (*IV*, *V*)—ν_0 = 14.01 MHz, H_0 13.46 kG).[33]

To assign the lines in spectra *II* and *V* (Fig.3) to various oppositions of the niobium atoms, a model calculation of the asymmetry parameter η_{as}, of the relative value of the frequency of the quadrupole coupling $\nu_Q/|q_C - q_\square|$ (where $|q_C - q_\square|$ is the absolute magnitude of the difference in the charges of the carbon atom and the vacancy, expressed in units of electron charge), and of the probabilities of the different positions of the niobium atoms $P_i^{disordered}$ and $P_i^{ordered}$ in the disordered and ordered states of $NbC_{0.83}$ respectively was carried out.[23,33,34] The results of the calculations[23,24] are given in Table 1. The large difference between $P_i^{disordered}$ and $P_i^{ordered}$ indicates that the NMR spectra of the disordered and ordered phases should differ considerably from one another. For example, for the disordered carbide $NbC_{0.83}$, the most probable positions are Nb_0^0 and Nb_0^1 (Fig.4) with a complete first coordination sphere, whereas for the ordered phase the most probable position is Nb_1^1 (Fig.4*b*), and there should be no niobium atom positions with a complete first coordination sphere.

In the comparison of the data on ν_Q and η_{as} obtained from the model calculation and from experiment, the authors cited[23] gave preference to the coincidence of the calculated and experimental values of the asymmetry parameters η_{as}^{calc} and η_{as}^{expt}. As a result of this comparison, they were able to find the experimental values of the hyperfine interaction parameters ν_Q, η_{as}, and *K* (Table 1) for different niobium atom positions.

By taking into account the environments of the niobium atoms with an accuracy up to three coordination spheres, the authors cited[23,33,34] were able to explain the presence of all the peaks in the ^{93}Nb NMR spectra of the carbide $NbC_{0.83}$. In the completely ordered $NbC_{0.83}$, only two types of position are possible, namely Nb_1^1 and Nb_1^2 (Figs.4*d* and 4*e*). The study of the carbides $NbC_{0.81}$ and $NbC_{0.88}$ showed that the nature of the short-range order in them is the same as in the monoclinic ordered phase Nb_6C_5 with space group $C2/m$.[37–40] Calculation of the Knight shifts showed that for niobium carbide, as for other non-stoichiometric compounds, the value of K increases with increase in the number of vacancies in the environment of the metal atom. The difference in the Knight shifts for different positions of the niobium atoms indicates a difference in the populations of their *d* orbitals for different immediate environments. Overall, the results obtained[23,33–36] indicate that the nature of the short-range order in niobium carbide, as in other non-stoichiometric compounds, is determined chiefly by the mutual repulsion of the vacancies in the non-metal sub-lattice.

2. The Study of Short-range Order by Diffuse Scattering

There are few published papers on the study of short-range order in non-stoichiometric compounds by diffuse scattering. Experimental data[45] on the intensity of the diffuse scattering of electrons by vanadium carbide $VC_{0.75}$ have been used[41–44] to calculate the parameters of the short-range order $\alpha(hkl)$ for the eight nearest coordination spheres of the non-metal sub-lattice; a vacancy was chosen as the centre of the coordination sphere. The results of the determination of the parameters α and the numbers of carbon atoms n_C and vacancies $n_\square$ in each coordination sphere are given in Table 2 (for comparison, the same quantities were calculated for the ordered phase V_6C_5 with a trigonal superstructure).

The data in Table 2 show that the nature of the distribution of the carbon atoms and vacancies in the non-metal sub-lattice of the carbide $VC_{0.75}$ differs considerably from the statistical distribution; for example, in the first two coordination spheres the number of vacancies is much smaller than that expected for the random distribution. With increase in the radius of the coordination sphere, the value of α oscillates, and its absolute magnitude gradually decreases. The results were attributed[43,44] to the mutual repulsion of the vacancies, and it was noted that analogous short-range order should be observed in niobium and tantalum carbides. The conclusion that there is similar short-range order in the non-stoichiometric monocarbides of the group V transition metals was also reached in Ref.46. According to Ref.46, it is impossible to obtain absolutely disordered (without short-range order) VC_y specimens with $y > 0.78$.

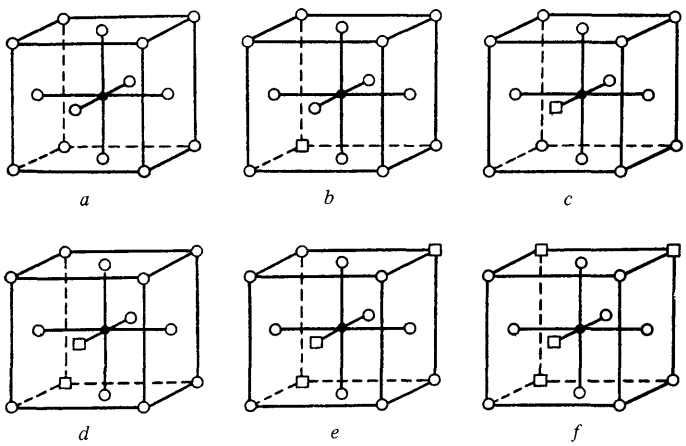


Figure 4. Most probable positions of the niobium atom in niobium carbide NbC*y*: (a) position Nb_0^0, (b) position Nb_0^1, (c) position Nb_1^0, (d) position Nb_1^1, (e) position Nb_1^2, (f) position Nb_1^3 (○—carbon atom, □—vacancy, ●—resonating niobium atom).

Table 1. Parameters of the ^{93}Nb NMR spectra of niobium carbide $NbC_{0.83}$ and the local environment of the niobium atoms.[23,33,34]

Nb position	Position symbol*	Position of vacancy**	Results of model calculations (Ref.23)				Unique points of the NMR spectrum***		Results of calculations from the NMR spectra (Refs.33, 34)			
			$\nu_Q/\lvert q_C-q_\square\rvert$, MHz	η_{as}^{calc}	$P_i^{disordered}$	$P_i^{ordered}$	$\nu_0=21.5$, MHz	$\nu_0=14.01$, MHz	ν_Q, MHz	η_{as}^{calc}	$\lvert q_C-q_\square\rvert$	K, %
Nb_0^0	*a*	—	0	0	0.09	0	*O*	*O*	0	—	—	−0.11±0.05
Nb_0^1	*b*	7	0.2	0	0.13	0	*O*, *O′*	*O*, *O′*	0.3±0.07	0	1.5	−0.11±0.05
Nb_0^2	—	7; 14	0.4	0	0.01	0	*O*	*O*	—	—	—	−0.11±0.05
Nb_0^2	—	7; 8	0.2	1.0	0.04	0	*O*	*O*	—	—	—	−0.11±0.05
Nb_0^2	—	7; 9	0.2	1.0	0.04	0	*O*	*O*	—	—	—	−0.11±0.05
Nb_1^0	*c*	1	1.05	0	0.10	0	*A*, *A′*	*A*, *A′*	1.9±0.3	0	1.8	−0.25±0.05
Nb_1^1	*d*	1; 7	1.05	0.2	0.07	0.66	*A*, *B′*	*A*, *B′*	2.0±0.3	0.2±0.05	1.9	−0.14±0.05
Nb_1^2	*e*	1; 7; 9	1.05	0.4	0.007	0.33	*B*, *O′*	*B*, *C′*	2.1±0.3	0.4±0.05	2.0	0.25±0.05
Nb_1^3	*f*	1; 7; 8; 9	1.05	0.6	0.001	0	*B*, *O′*	*B*, *D′*	2.2±0.3	0.5±0.10	2.1	0.50±0.10
Nb_2^0	—	1; 4	2.1	0	0.01	0	—	—	—	—	—	—

*See Fig.4.
**See Fig.1.
***See Fig.3.

Short-range order has been studied by the diffuse scattering of neutrons by the carbides $TiC_{0.76}$ and $NbC_{0.73}$.[47] The distribution of the intensity of the diffuse scattering of neutrons by single crystals of carbides with the composition indicated was measured at room temperature in the $(1\bar{1}0)$ plane of the reciprocal lattice in the range of change in the modulus of the diffraction vector $0.2\ Å^{-1} < 2\pi q < 4\ Å^{-1}$. Before the measurements, the single crystals of $TiC_{0.76}$ and $NbC_{0.73}$ were annealed in a vacuum for several days. The values obtained for the intensity of the diffuse scattering indicate that the atoms are displaced from the positions of the ideal undistorted lattice. A Fourier transformation was used[47] to determine the short-range order parameter α for the eight nearest coordination spheres of the non-metal sub-lattice of these carbides (Table 2). The data given in Table 2 show that the nature of the distribution of the vacancies in $TiC_{0.76}$ and $NbC_{0.73}$ is fundamentally the same, and, as in VC_y, is due to the mutual repulsion of vacancies. It was also noted[47] that the correlations in niobium carbide extend to more than nine coordination spheres. The results[47] show qualitative agreement with data obtained[46] in a study of NbC_y powders by the diffuse scattering of neutrons.

Table 2. Parameters of the short-range order and the distribution of the carbon atoms and vacancies in the carbide $VC_{0.75}$, the ideal ordered phase V_6C_5, and the carbides $NbC_{0.73}$ and $TiC_{0.76}$.

hkl	*N*	$VC_{0.75}$ (Ref.43)			V_6C_5 (Ref.43)			$NbC_{0.73}$ (Ref.47)			$TiC_{0.76}$ (Ref.47)		
		α	n_C	$n_\square$	α	n_C	$n_\square$	α	n_C	$n_\square$	α	n_C	$n_\square$
110	12	−0.178	10.6	1.4	−0.2	12	0	−0.095	9.6	2.4	−0.005	9.2	2.8
200	6	−0.260	5.7	0.3	−0.2	6	0	−0.275	5.6	0.4	−0.080	4.9	1.1
211	24	0.176	14.8	9.2	0.2	16	8	0.051	16.6	7.4	0.013	18.0	6.0
220	12	0.008	8.9	3.1	0	10	2	0.072	8.1	3.9	0.006	9.1	2.9
310	24	0.041	17.3	6.7	0	20	4	0.044	16.7	7.3	−0.003	18.3	5.7
222	8	−0.171	7.0	1.0	−0.2	8	0	−0.030	6.0	2.0	0.025	5.9	2.1
321	48	−0.070	38.5	9.5	−0.1	44	4	−0.020	35.7	12.3	−0.007	36.7	11.3
400	6	0.143	3.8	2.2	0.2	4	2	0.030	4.2	1.8	0.003	4.5	1.5

Notation: N is the number of sites in the coordination sphere (hkl).

The study of polycrystalline specimens of $ZrC_{0.80}$ and $ThC_{0.75}$ by the diffuse scattering of neutrons[46] made it possible to determine the correlations in the distribution of the vacancies in three coordination spheres (with a vacancy at the centre). According to these data, the first coordination sphere contains a small number of vacancies (smaller than that for the statistical distribution), the second coordination sphere contains no vacancies, and the third coordination sphere contains many more vacancies than for the random distribution ($\alpha_1 = -0.05$, $\alpha_2 = -0.20$, $\alpha_3 = 0.075$).

The diffuse scattering of electrons has been used to study short-range order in the lower carbides of vanadium and niobium V_2C and Nb_2C.[48] The short-range and long-range order in these compounds was related to the distribution of the interstitial atoms in regular rows $C-\square-C-\square-\ldots$ parallel to the c axis. Comparison of the experimental and calculated values of the intensity of diffuse scattering established the possible types of order in Nb_2C and V_2C.[48]

Overall, the available published data on short-range order in the non-metal sub-lattice of non-stoichiometric compounds indicate that the correlations in the distribution of the interstitial atoms and vacancies have been studied comparatively effectively only in the compounds of vanadium and niobium; the carbides of these metals have been studied in most detail. The nature of the short-range order in the non-metal sub-lattice of non-stoichiometric carbides is due mainly to the repulsion of vacancies. In the carbides of the group V transition metals, the sites of the first two coordination spheres (with a vacancy at the centre) are occupied chiefly by carbon atoms, whereas the vacancies are present mainly in the third coordination sphere; this type of short-range order corresponds to the distribution of the atoms in ordered phases of the type M_6C_5. In the carbides of the group IV transition metals, the nature of the short-range order is related to the fact that the second coordination sphere contains practically no vacancies, while the third coordination sphere contains large numbers of vacancies. The short-range order in the lower hexagonal carbides and nitrides M_2X is due to the formation of rows $X-\square-X-\square-\ldots$ directed along the c axis.

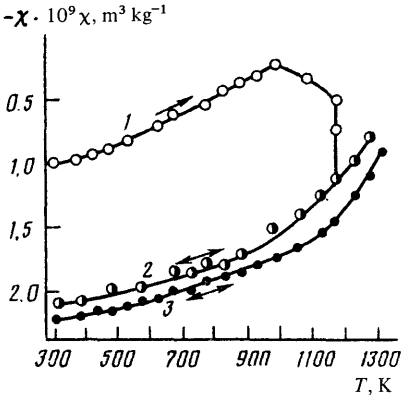


Figure 5. Influence of ordering on the magnetic susceptibility χ of niobium carbide $NbC_{0.83}$ (the arrows indicate the direction of the change in temperature): (1) quenched disordered carbide (2) carbide ordered during the measurement of the susceptibility, (3) annealed ordered carbide.[23,50]

3. The Study of Short-range Order by Magnetic Susceptibility

Magnetic susceptibility was first used to analyse the distribution of the atoms in a crystal and to determine short-range order in studies[23,49-51] of the non-stoichiometric niobium carbide NbC_y.

Measurements of the magnetic susceptibility χ of niobium carbide specimens with different compositions in the temperature range 300−1300 K showed that the value of χ depends on the nature of the thermal treatment of the carbide NbC_y ($0.81 \leqslant y \leqslant 0.88$). For specimens which were quenched from temperatures appreciably higher than the temperature of the disorder−order transition and which gave neutron diffraction patterns with no superstructural reflections, an abrupt decrease in χ was observed (Fig.5) to values characteristic of ordered specimens with the same composition, obtained by the methods of Refs.23 and 37. The neutron diffraction patterns recorded after the $\chi(T)$ measurements showed superstructural reflections, indicating that ordering of the structure takes place during the measurements. It was also found that the values of χ are the same for specimens containing the disordered and ordered phases simultaneously and for NbC_y specimens with the

same composition containing only the ordered phase, that is the susceptibility is independent of the concentration of the ordered phase. Since the production of long-range order is accompanied by the production of short-range order, the fact that χ is independent of the concentration of the ordered phase, and the change in χ on thermal treatment, indicate that the magnetic susceptibility is determined chiefly by the production of short-range and not long-range order.

The idea that short-range order has a definite influence on the magnitude of the magnetic susceptibility was confirmed by the calculation[23,49,50] of the short-range order parameters from experimental data.[23] The essential features of the calculation were as follows. Firstly, the $\chi(T)$ relationships for NbC_y specimens with different compositions in the disordered and ordered states were used to determine by the published method[49] the values of $P_i(y)$, the probabilities of existence in the NbC_y crystal of niobium atom positions with the i-th configuration of the carbon atoms, and the vacancies forming the immediate environment of the metal atom.

According to Refs.23, 49, and 50, for a correct description of the carbide MC_y in the composition range $1.0 \geqslant y \geqslant 0.80$ it is sufficient to consider only four positions: the position with a complete metal atom environment, having a probability P_0; the position with one vacancy in the octahedral environment of the metal atom, having a probability P_1; and positions with two non-adjacent and adjacent vacancies, having probabilities P_2 and P_3 respectively.

The short-range order parameter α_j in the j-th coordination sphere of the non-metal sub-lattice can be determined from the equation:[23]

$$\alpha_j = 1 - P^{(j)}_{C-\square}/P^{bin}_{C-\square}, \quad (4)$$

where $P^{(j)}_{(C-\square)}$ and $P^{bin}_{(C-\square)}$ are the probabilities of formation of the pair $C-\square$ in the compound being studied and in the completely disordered compound. For the carbide MC_y the binomial probability is $\lambda_{C-\square}P^{bin}_{C-\square} = 2y(1-y)$, and the actual probability of formation of the pair $C-\square$ in the j-th coordination sphere can be found from the known probability $P_i(y)$ using the equation:

$$\lambda_{C-\square}P^{(j)}_{C-\square} = \sum_i n_i^{(j)}\lambda_i P_i(y), \quad (5)$$

where $n_i^{(j)}$ is the relative fraction of $C-\square$ pairs in the j-th coordination sphere of the position of the metal atom with the i-th configuration; $\lambda_{C-\square} = 2$ is the multiplicity of the $C-\square$ pair; and λ_i is the multiplicity of the i-th configuration of the immediate environment of carbon atoms and vacancies round the metal atom (the multiplicity of a given group of atoms is the number of its equivalent configurations, which are brought into coincidence with one another by symmetry transformations). In the examination of the above four metal atom positions,

$$\lambda_{C-\square}P^{(1)}_{C-\square} = \lambda_1 P_1(y)/3 + 2\lambda_2 P_2(y)/3 + \lambda_3 P_3(y)/2$$

and

$$\lambda_{C-\square}P^{(2)}_{C-\square} = \lambda_1 P_1(y)/3 + 2\lambda_3 P_3(y)/3.$$

The calculation showed that for NbC_y specimens in the disordered state, the values of α_1 and α_2 are close to zero, whereas for the annealed specimens, the values of α_1 and α_2 are negative and differ considerably from zero; for example, for the annealed carbides $NbC_{0.88}$, $NbC_{0.83}$, and $NbC_{0.81}$, the parameters α_1 and α_2 have the values −0.064 and −0.040, −0.132 and −0.126, and −0.153 and −0.137 respectively. The negative values of α_1 and α_2 indicate the mutual repulsion of particles of the same kind, which also determines the nature of the short-range order in the non-metal sub-lattice of niobium carbide.

Magnetic susceptibility has also been used[52] to study the ordering in non-stoichiometric tantalum carbide TaC_y. The temperature dependence $\chi(T)$ for tantalum carbide specimens in the disordered and ordered states was similar to that observed[23,50] for niobium carbide. The experimentally measured magnetic susceptibility of tantalum carbide was used[52] to calculate the short-range order parameters. According to the calculation, the parameters in the first and second coordination spheres of the non-metal sub-lattice of ordered tantalum carbide are non-zero: $\alpha_1 = -0.086$ and $\alpha_2 = -0.054$ for $TaC_{0.83}$, and $\alpha_1 = -0.076$ and $\alpha_2 = -0.020$ for $TaC_{0.85}$.

For ideal ordered phases of the type $M_6C_5(MC_{0.83})$, $\alpha_1 = \alpha_2 = -0.20$,[49] in good agreement with the values obtained for $TaC_{0.83}$. The slight differences between the values of α_1 and α_2 calculated from the magnetic susceptibility and the limiting possible values of these parameters indicate that complete ordering was not achieved in the niobium and tantalum carbide specimens studied in Refs.49–52.

Overall, the results of the study of the short-range order in niobium and tantalum carbides by magnetic susceptibility[23,49–52] show good agreement with one another and with the results of NMR studies of the short-range order in non-stoichiometric carbides of the group V transition metals.

III. SHORT-RANGE ORDER IN CARBIDE SOLID SOLUTIONS

In the works discussed, the short-range order was studied in the non-metal sub-lattice of the non-stoichiometric compounds. The results of the study of the atom distribution in the metal sub-lattice of solid solutions of non-stoichiometric compounds of various transition metals are of considerable theoretical and practical interest.

The diffuse scattering of X-rays has been used repeatedly to study the short-range order in the metal sub-lattice of solid solutions formed by transition metal carbides with compositions close to the stoichiometric. In the opinion of Iveronova and Katsnel'son,[53] the most significant results of the study of short-range order in solid solutions M^1C-M^2C is the actual establishment of the fact that the distribution of the metal atoms in the sites of the metal sub-lattice is not random, and the detection of the influence of carbon on the nature of the correlations in the arrangement of the metal atoms.

The first studies of the local distribution of the atoms in the metal sub-lattice of the solid solutions NbC–TaC and ZrC–HfC with the equimolar composition were described in Refs.54–56. The absence of vacancies in the carbon sub-lattice and the similarity of the atomic radii of the metals replacing one another (Nb, Ta, Zr and Hf) made it possible to assume the absence of static distortions in the lattice of the solid solution. The short-range order parameters for the three nearest coordination spheres were calculated from the measured intensities of the diffuse scattering. For the first and second coordination spheres, the values of the short-range order parameters were found to be positive, and α_1 and α_2 increased with decrease in the temperature of quenching or annealing (Table 3). The positive values of α_1 and α_2 indicate that in the first and second coordination spheres of the metal atoms of a given kind, the concentration of metal atoms of the same kind is higher than that for the statistical distribution, that is there is short-range order involving short-range separation into layers. Short-range separation into layers has also been observed in Nb–Ta alloys.[57]

The short-range order parameter α_3 for the third coordination sphere is negative and close to zero, so that the correlations in the arrangement of the atoms in the metal sub-lattice apparently extend to only two coordination spheres. Additional annealing of the specimens of the solid solutions, and also the addition of 1 mole % WC, led to an increase in the correlations in the relative arrangements of the metal atoms.[54-56]

Table 3. Parameters of the short-range order in the metal sub-lattice of carbide solid solutions and in alloys.

Composition	T, K	Short-range order parameters			Refs.
		α_1	α_2	α_3	
$Nb_{0.5}Ta_{0.5}C$*	2000	0.058	0.025	$\leqslant 0$	[54]
$Nb_{0.5}Ta_{0.5}C$*	1800	0.089	0.049	$\leqslant 0$	[54]
$Nb_{0.5}Ta_{0.5}C$*	1500	0.120	0.071	$\leqslant 0$	[54]
$Nb_{0.5}Ta_{0.5}C$ + 1 mole % WC*	1800	0.11	0.10	0.02	[56]
$Nb_{0.5}Ta_{0.5}C$ + 1 mole % WC*	1500	0.14	0.13	0.04	[56]
$Nb_{0.5}Ta_{0.5}$	1600	0.13	0.09	0.02	[57]
$Nb_{0.5}Ta_{0.5}$*	1400	0.16	0.08	−0.04	[57]
$Zr_{0.5}Hf_{0.5}C$	2200	0.06	>0	$\leqslant 0$	[55]
$Zr_{0.5}Hf_{0.5}C$	1800	0.09	>0	$\leqslant 0$	[55]
$Nb_{0.5}Ti_{0.5}C$	2200	−0.06	—	—	[53,58,59]
$Nb_{0.75}Ti_{0.25}$	1500	0.066	0.103	—	[60]
$Nb_{0.5}Ti_{0.5}$	1500	0.063	0.047	—	[60]
$Nb_{0.25}Ti_{0.75}$	1500	0.091	0.017	—	[60]
$Ti_{0.5}Ta_{0.5}C$	2200	−0.06	—	—	[53.58.59]
$Ti_{0.5}Ta_{0.5}$	1500	0.19	—	—	[53.58.59]
$Ti_{0.5}Zr_{0.5}C$	—	0.07	—	—	[53]
$Ti_{0.5}Hf_{0.5}C$	—	0,03	—	—	[53]
$V_{0.5}Nb_{0.5}C$	2100	0.01	—	—	[53,58,59]
$V_{0.44}Nb_{0.56}$	—	−0,23	—	—	[53,58,59]
$V_{0.5}W_{0.5}C$	2100	0.03	—	—	[53,58,59]
$V_{0.65}W_{0.35}$	—	−0.10	—	—	[53.58.59]
$Ti_{0.5}W_{0.5}C$	2200	−0.06	—	—	[53.58,59]
$Ti_{0.61}W_{0.39}C_{0.98}$	2400	−0.09	0.03	0	[63]
$Ti_{0.77}W_{0.23}C_{0.88}$	2400	−0 07	0	0	[63]
$Ti_{0.84}W_{0.16}C_{0.98}$	2400	−0,06	0,02	0.01	[63]
$Ti_{0.91}W_{0.09}C_{0.98}$	2400	−0.05	−0,02	−0.02	[63]
$Ti_{0.58}W_{0.42}C_{0.94}$	2400	−0 06	0.04	0	[63]
$Ti_{0.59}W_{0.43}C_{0.86}$	2400	0,05	0.16	0.04	[63]
$Ti_{0.59}W_{0.41}C_{0.78}$	2400	0,07	0,15	0,03	[63]

*Specimens subjected to thermal treatment by annealing; in the other cases by quenching.

Diffuse scattering has been studied[58,59] in the solid solutions with the equimolar composition TiC−NbC, TiC−TaC, TiC−WC, VC−NbC, and VC−WC, and in the alloys Ti−Ta with the equiatomic composition, V−Nb (36 at.% Nb), and V−W (35 at.% W). The short-range order parameter α_1 is positive for the Ti−Ta alloys, and negative for the V−Nb and V−W alloys. For all the carbide solid solutions studied except VC−WC, $\alpha_1 < 0$; for VC−WC, $\alpha_1 > 0$. Comparison of the values of α_1 in the carbide solid solutions and in the corresponding metal alloys shows that in the solid solutions TiC−NbC, VC−WC, and TiC−TaC, the sign of α_1 is the opposite of that for the alloys Ti−Nb,[60] V−W, and Ti−Ta (Table 3).

The short-range order in TiC−WC solid solutions was studied in Refs.61−63. The intensity of the diffuse scattering of X-rays was measured using specimens with different compositions subjected to thermal treatment under slightly different conditions (sintering at different temperatures, quenching, gradual cooling in the furnace, etc.). According to the results, in all the specimens of the TiC−WC solid solutions with a complete carbon sub-lattice, $\alpha_1 < 0$, and for the second and third coordination spheres the parameters α_2 and α_3 are close to zero (Table 3). This means that the correlations in the arrangements of the titanium and tungsten atoms are observed at short distances within 1−3 coordination spheres. In all cases, additional annealing of the specimens led to an increase in the absolute magnitude of the short-range order parameters. States with a metal atom distribution close to the statistical distribution were not detected.

Increase in the tungsten concentration in the TiC−WC solid solutions is accompanied by an increase in the degree of short-range order in the first coordination sphere. The nature of the distribution of the metal atoms is influenced considerably by the carbon concentration. When the carbon concentration deviates from the stoichiometric, the short-range order parameters for the three nearest coordination spheres become positive (Table 3). At the same time, the nature of the diffuse scattering of X-rays by non-stoichiometric solid solutions indicates that there are two types of short-range order in their structures: with $\alpha_1 < 0$ and with $\alpha_1 > 0$. The authors cited[61-63] therefore suggested that in the non-stoichiometric solid solution $Ti_xW_{1-x}C_y$, in addition to the formation of segregations of the atoms of one metallic element, regions of short-range order with the structure typical of the stoichiometric solid solution are preserved.

IV. LOCAL DISPLACEMENTS OF THE ATOMS

In the disordered state, non-stoichiometric compounds are characterised by a random distribution of the interstitial atoms and vacancies in the sites of the non-metal sub-lattice, and therefore do not have the translational symmetry of the crystal with the stoichiometric composition. As a consequence of this random distribution, however, the probabilities of occupancy of the sites of the non-metal sub-lattice are equal, so that all these sites are crystallographically equivalent. In other words, in disordered non-stoichiometric compounds there is translational symmetry of a lattice of site occupancy probabilities.

Most non-stoichiometric compounds with wide homogeneity ranges have a highly symmetrical structure of the NaCl type, which is preserved for the disordered distribution of the interstitial atoms and vacancies. A result of the disordered distribution is the loss of the symmetry of the local environment of each atom. The distortion of the local symmetry leads in turn to static displacements of both the metal atoms and the interstitial atoms. The static displacements are the deviations of the atoms from the positions corresponding to the ideal basic structure of the compound, that is they represent the quantity $\mathbf{u}_n = \mathbf{R}_n - \mathbf{r}_n$, where $\mathbf{R}_n$ and $\mathbf{r}_n$ are the radius-vectors defining the position of the atom n in the real and ideal lattices respectively. Unlike the dynamic displacements, due to the thermal vibrations of the atoms, the static displacements result from the difference in the energies of the bonds between neighbouring atoms.

The cubic symmetry of disordered non-stoichiometric compounds allows only a spherically symmetrical distribution of the static displacements of the atoms, since otherwise the crystallographic equivalence of different sites of the crystal would be destroyed. In disordered non-stoichiometric compounds, the symmetrical distribution of the static displacements is ensured by the random distribution of the vacancies. By taking account of the radial distribution of the

static displacements and making use of the analogy with dynamic displacements, it is possible to examine the mean-square static displacements.

During ordering, the symmetry of the crystal is lowered, and is accompanied by a change in the symmetry of the local environment of the atoms (for the stoichiometric composition of the ordered phase, the symmetry of the local environment coincides with the crystal symmetry). Since in the ordered state the symmetry of the local environment is not cubic, ordering must be accompanied by static displacements of the atoms. The magnitude of the static displacements is different for the disordered and ordered states of a crystal, since the local environments of the atoms are different in these states.

The determination of the magnitude and direction of the static displacements for each atom in non-stoichiometric compounds with different structural states makes it possible to find the equilibrium positions, that is to determine the crystal structure more accurately and completely. Comparison of the values of the static displacements corresponding to different structural states can also be used to investigate possible mechanisms of phase transformations of the order–disorder type and to analyse the nature of the change in the inter-particle interactions in a crystal during ordering.

The principal methods for determining the displacements of atoms are by the diffraction of X-rays and thermal neutrons. There is no fundamental difference between these methods, since the elastic scattering of neutrons at the nuclei of the atoms and the scattering of X-rays on the static imperfections of the crystal are described by essentially identical equations and can be examined using the same theory.[64,65] At the same time, the difference in the parameters of the theory may lead to extremely significant methodological advantages.

The amplitudes of the scattering of X-rays by individual atoms are determined by the number of electrons in them, and increase regularly with increase in the atomic number of the element in the periodic system, whereas the amplitudes of the scattering of neutrons by the nuclei of different atoms change in irregular fashion. For non-stoichiometric compounds such as the transition metal carbides and nitrides, this means that in the scattering of X-rays, the main contribution to the intensity of the diffraction peaks will be made by the transition metal atoms, so that when X-ray diffraction is used to determine displacements, the information on the non-metal sub-lattice is practically completely lost. In neutron diffraction, the amplitudes of the atomic scattering of the neutrons by different components of non-stoichiometric compounds are of comparable magnitude (for example, for zirconium, hafnium, niobium, tantalum, carbon, and nitrogen, the amplitudes of the scattering of neutrons are 0.71×10^{-12}, 0.78×10^{-12}, 0.71×10^{-12}, 0.70×10^{-12}, 0.665×10^{-12}, and 0.94×10^{-12} cm respectively[66]). Thus when the diffraction of thermal neutrons is used, contributions to the intensity of the observed reflections are made by both the metal atoms and the non-metal atoms. The determination of displacements by neutron diffraction is in general more accurate than that by X-ray diffraction, since the amplitude of the scattering of neutrons is independent of the angle of scattering, and it is not necessary to introduce a correction for extinction; moreover, the absorption of neutrons by a substance is much less than the absorption of X-rays. Thus neutron diffraction is preferred for determining displacements in non-stoichiometric compounds of transition metals.

The decrease in the intensity of the diffraction lines is due to both dynamic (thermal) and static displacements of the atoms from the sites of the ideal crystal lattice, and in the absence of ordering these two factors bring about a decrease in intensity according to the same law.[64,67] In fact, the presence of dynamic displacements means that the positions of the atoms are time-dependent, but since the frequency of the scattered radiation is several orders of magnitude greater than the frequency of the thermal vibrations of the atoms, it can be assumed that the scattering takes place on stationary atoms occupying certain instantaneous positions. From this it follows that for the diffraction experiment there is no fundamental difference between dynamic and static displacements; it is necessary only to consider their superposition, as a result of which the intensity of the spectrum will depend on the sum of their mean-square values:

$$\langle U_{\Sigma}^2 \rangle = \langle U_{\text{st}}^2 \rangle + \langle U_{\text{dyn}}^2 \rangle. \qquad (6)$$

The dynamic displacements can be separated from the total displacements, for example, by using the temperature dependence of the intensities of the diffraction lines.

At present, static displacements have been determined only for several transition metal carbides and nitrides; almost all the studies have been carried out only with compounds in the disordered state.

X-Ray diffraction has been used[68] to determine the displacements $< U_{\Sigma}^2 >$ of the atomic complex MX_y in the homogeneity ranges of the carbides of titanium, zirconium, and hafnium. The recording was carried out at room temperature, at which, in the opinion of the authors cited, the thermal vibrations of the atoms are small and the dynamic displacements can be neglected. Thus it was assumed[68] that $< U_{\Sigma}^2 > \simeq < U_{\text{st}}^2 >$. Increase in the defect character of the carbon sub-lattice was accompanied by a marked increase in the static distortions of the lattice (Table 4). The greatest static displacements are observed for titanium carbide; the magnitude of the displacements decreases on going to zirconium and hafnium carbides. Comparison of the nature of the change in the crystal lattice constants and the displacements with change in the composition of the carbides indicated that a sharper change in the crystal lattice constant with change in composition is accompanied by larger static distortions.

Neutron diffraction has been used[69] to determine the static displacements in the carbides of titanium, zirconium, vanadium, niobium, and tantalum. The effective mean-square displacements were found from the experimentally determined intensities of the diffraction reflections. For carbides MC with compositions close to the stoichiometric, the static distortions should be small, since the lattice is practically complete; thus for the stoichiometric compositions, $< U_{\Sigma}^2 > = < U_{\text{dyn}}^2 >$. Evidence in support of this is provided by the good agreement between the values obtained for $< U_{\Sigma}^2 >$ and the values of $< U_{\text{dyn}}^2 >$ calculated[70] from the elastic constants in the Debye approximation ($< U_{\text{dyn}}^2 >^{1/2}$ has the values 0.081 Å for TiC, 0.069 Å for ZrC, and 0.072 Å for NbC). The authors cited[69] assumed that the Debye temperature depends little on the composition of the carbides, and hence that the dynamic distortions of the lattice change little with decrease in the carbon concentration and that in a first approximation their dependence on the composition of the carbide MC_y can be neglected. This makes it possible to calculate the static displacements from the equation:

$$\langle U_{\text{st}\,MC_y}^2 \rangle = \langle U_{\Sigma\,MC_y}^2 \rangle - \langle U_{\text{dyn}\,MC}^2 \rangle = \langle U_{\Sigma MC_y}^2 \rangle - \langle U_{\Sigma MC}^2 \rangle. \qquad (7)$$

The values obtained[69] for the displacements for titanium carbide were much lower than those obtained[68] by X-ray diffraction; the data[68,69] for zirconium carbide show better agreement (Table 4).

Neutron diffraction has been used[71] to determine the mean-square displacements of the atomic complex MN and the metal and nitrogen atoms, $< U_{\Sigma MN}^2 >$, $< U_{\Sigma M}^2 >$, and $< U_{\Sigma N}^2 >$, in the nitrides

$TiN_{0.98}$, $ZrN_{1.00}$, and $HfN_{0.98}$ with compositions close to the stoichiometric (Table 4). The results for titanium and zirconium nitrides agree satisfactorily with calculated data[72] obtained from the elastic constants in the Debye approximation ($<U^2_{dyn}>^{1/2}$ has the values 0.083 Å for TiN and 0.080 Å for ZrN).

Table 4. Mean-square displacements (Å) in non-stoichiometric compounds of transition metals MX_y.

Composition	$\langle U^2_{st\,MX_y}\rangle^{1/2}$	$\langle U^2_{ct\,MX_y}\rangle^{1/2}$	$\langle U^2_{\Sigma M}\rangle^{1/2}$	$\langle U^2_{\Sigma X}\rangle^{1/2}$	Refs.
$TiC_{0.82}$	—	0.160	—	—	[68]
$TiC_{0.66}$	—	0.184	—	—	[68]
$TiC_{0.50}$	—	0.199	—	—	[68]
$TiC_{0.96}$	0.084	—	—	—	[69]
$TiC_{0.86}$	0.104	0.065	—	—	[69]
$TiC_{0.81}$	0.119	0.087	—	—	[69]
$TiC_{0.65}$	0.142	0.118	—	—	[69]
$TiC_{0.96}$	0.103	—	0.084	0.109	[74]
$ZrC_{0.80}$	—	0.066	—	—	[68]
$ZrC_{0.70}$	—	0.120	—	—	[68]
$ZrC_{0.60}$	—	0.138	—	—	[68]
$ZrC_{0.97}$	0.075	—	—	—	[69]
$ZrC_{0.93}$	0.101	0.067	—	—	[69]
$ZrC_{0.87}$	0.110	0.080	—	—	[69]
$ZrC_{0.67}$	0.142	0.120	—	—	[69]
$ZrC_{0.63}$	0.147	0.126	—	—	[69]
$HfC_{0.90}$	—	0.080	—	—	[68]
$HfC_{0.70}$	—	0.091	—	—	[68]
$HfC_{0.60}$	—	0.095	—	—	[68]
$VC_{0.845}$	0.096	0.045	—	—	[69]
$VC_{0.814}$	0.106	0.063	—	—	[69]
$NbC_{1.0}$	0.081	—	—	—	[69]
$TaC_{1.0}$	0.091	—	—	—	[69]
$TiN_{0.98}$	0.089	—	0.078	0.100	[71]
$TiN_{0.98}$	0.105	—	0.081	0.096	[74]
$ZrN_{1.0}$	0.085	—	0.061	0.112	[71]
$HfN_{0.98}$	0.081	—	0.049	0.126	[71]
$TiC_{0.48}N_{0.51}$	0.107	—	—	—	[74]

The magnitude and direction of the relative static displacements of the atoms in the carbides $ZrC_{0.64}$,[46] $TiC_{0.76}$, and $NbC_{0.73}$ [47] have been determined by the diffuse scattering of neutrons. In $ZrC_{0.64}$, the zirconium atoms are displaced from the vacancies by 0.04 Å. In titanium and niobium carbides, the metal atoms are also displaced from the vacancy towards the carbon atom by 0.030 Å and 0.033 Å respectively, whereas the carbon atoms move away from one another (in the first coordination sphere of the non-metal sub-lattice, the distance between neighbouring carbon atoms increased by 0.011 Å in $TiC_{0.76}$ and by 0.006 Å in $NbC_{0.73}$).

The local displacements of the atoms situated round the carbon vacancy in NbC_y ($0.05 \leqslant y \leqslant 0.12$) have been determined[73] by an X-ray diffraction study of single crystals. To distinguish the dynamic and static displacements, the X-ray spectra of $NbC_{0.88}$ and $NbC_{0.93}$ were recorded at 299 K and 479 K. This made it possible to find the average Debye–Waller thermal factor for the temperature range indicated, equal to $2M = \ln(I_{479}/I_{299})$. According to the data obtained,[73] the magnitude of the dynamic displacements $<U^2_{dyn}>$ decreases with increase in the number of vacancies in the carbon sub-lattice of NbC_y, and can be described by the linear relationship

$$\langle U^2_{dyn}\rangle = 0.0027 - 0.005\,(1-y),\ \text{Å}^2. \qquad (8)$$

Since X-ray diffraction makes it possible to obtain information only on the metal sub-lattice, the authors cited[73] suggested that the vacancy is surrounded by six niobium atoms in the first and eight niobium atoms in the second coordination spheres, and that the displacement of the metal atoms in the subsequent coordination spheres and the displacements of the carbon atoms do not lead to a change in the X-ray diffraction patterns. It was also assumed that the vacancies are situated at an appreciable distance from one another, so that the position of the niobium atoms is influenced by only one vacancy. This assumption is applicable only for niobium carbide compositions close to the stoichiometric, and is not applicable to the $NbC_{0.88}$ specimen studied in Ref.73.

The static displacements of the niobium atoms for the first and second coordination spheres of a vacancy are $<U^2_{st}>_1 = 0.125$ Å and $<U^2_{st}>_2 = 0.009$ Å^2 respectively.[73] The directions of the displacements were also found; the niobium atoms in the first coordination sphere are displaced away from the vacancy, and those in the second coordination sphere are displaced towards the vacancy. Although the displacements of the niobium atoms in the second coordination sphere are much smaller than those in the first coordination sphere, the authors cited[73] assume that the displacements $<U^2_{st}>_2$ compensate the displacements in the first coordination sphere and lead to a decrease in the lattice constant of niobium carbide with increase in the concentration of vacancies. This interpretation of the experimental data appears doubtful, since in the work cited the coordinates of the carbon atoms were not determined, and the information on the positions of the niobium atoms is incomplete, that is there is practically no information on the crystal lattice constant.

The displacements $<U^2_{\Sigma MX_y}>$, $<U^2_{\Sigma M}>$, and $<U^2_{\Sigma X}>$ in titanium carbide $TiC_{0.96}$, titanium nitride $TiN_{0.98}$, and titanium carbide nitride $TiC_{0.48}N_{0.51}$ have been determined by neutron diffraction.[74] The authors cited give the values of the quantity $B = 8\pi^2 <U^2>/3$, from which the present authors calculated the values of the mean-square displacements $<U^2>$ (Table 4). The values of the displacements for titanium carbide and nitride show good agreement with the data of Refs.69 and 71, which were also obtained by neutron diffraction. In the study of titanium carbide in Ref.74, no deviations of the intensities of the diffraction reflections from the values calculated using the model of random displacements of the atoms from the positions of the ideal lattice were detected.

The displacements of the atoms in the homogeneity range of the disordered carbide NbC_y ($0.75 \leqslant y \leqslant 1.00$) have been studied in detail by neutron diffraction.[23,75,76] The presence of structural vacancies in non-stoichiometric niobium carbide brings about distortion of the symmetry of the local environment of the sites of the crystal lattice, and leads unavoidably to static displacements of both the atoms of the metallic matrix and the carbon atoms. When a special thermal treatment[23] ensuring a statistical distribution of the structural vacancies in the crystal lattice of the carbide is used, the symmetry of the carbide remains the same as that of the lattice of the defect-free carbide $NbC_{1.00}$, that is the disordered non-stoichiometric carbide NbC_y has an "average" highly symmetrical lattice, whose parameters change with change in composition. In this case the static distortions can be represented by the mean-square static displacements of the atoms, measured from the sites of this "average" lattice.

X-Ray diffraction[23] established that the concentration dependence of the cubic unit cell parameter of the disordered carbide NbC_y ($0.75 \leqslant y \leqslant 1.00$) is appreciably non-linear, with a point of inflection in the region of the composition $NbC_{0.83}$ (curve *1* in Fig.6).

In Refs.75 and 76, the mean-square static and dynamic displacements of the atoms were determined by neutron diffraction. The amplitudes of the scattering of neutrons by niobium and carbon atoms are of similar magnitude, and in this case the influence of the disordered displacements of the atoms on the diffraction effects can be taken into account using a Debye–Waller factor averaged over the atoms of different elements.[64,65,77] In a first approximation, the quantity M in the Debye–Waller factor can be regarded as a linear function of the displacements $< U_{\Sigma}^2 >$:[77]

$$M = 2\pi^2 q^2 \langle U_{\Sigma}^2 \rangle / 3, \qquad (9)$$

where

$$q = |\mathbf{q}| = 2 \sin[\theta(hkl)]/\lambda$$

is the length of the vector of the reciprocal lattice.

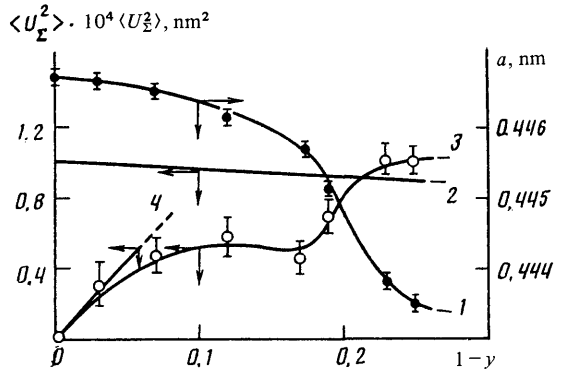


Figure 6. Changes in the crystal lattice parameter (1) and the dynamic (2) and static (3) mean-square displacements of the atoms in disordered niobium carbide NbC_y and the approximation of the static displacements (4) by Eqn.(11) in the range of low concentrations of vancancies.[76]

Measurement of the intensity of the diffraction peaks on the neutron diffraction patterns of the specimens of disordered NbC_y and construction of the $M = f(q^2)$ relationships, however, showed that they are non-linear at high values of q^2,[75,76] and the deviation from linearity takes place towards an increase in M for all niobium carbide specimens studied. Since a deviation of the $M = f(q^2)$ relationship from linearity is also characteristic of stoichiometric niobium carbide, the observed deviations were attributed[75,76] to the anharmonicity of the lattice vibrations of the atoms in niobium carbide. This conclusion agrees with the results of a study of the heat capacity of disordered niobium carbide,[78,79] where appreciable anharmonic effects were observed at $T \simeq 300$ K.

The contributions of the dynamic and static displacements of the atoms to $< U_{\Sigma}^2 >$ were distinguished[75,76] using the concentration dependence of the dynamic displacements of the niobium and carbon atoms in NbC_y, found from data on the low-temperature heat capacity

$$\langle U_{\text{dyn}}^2 \rangle = [0.010 - 0.004(1-y)] \times 10^{-2} \text{ nm}^2, \qquad (10)$$

which indicates larger values of the dynamic displacements than in Ref.73. According to Eqn.(10), increase in the concentration of structural vacancies in niobium carbide is accompanied by a decrease in the magnitude of the dynamic displacements (curve *2* in Fig.6). This can be attributed to a change in the contribution of the displacements of the carbon atoms as a result of the decrease in the carbon concentration when the niobium carbide composition deviates from the stoichiometric.

Data on the total mean-square displacements of the atoms $< U_{\Sigma}^2 >$ in NbC_y and the concentration dependence (10) of the dynamic displacements were used to determine the dependence of the mean-square static displacements $< U_{\text{st}}^2 >$ on the niobium carbide composition (curve *3* in Fig.6). The magnitude of the static displacements increases when the niobium carbide composition deviates from the stoichiometric; a local minimum is observed for the specimen $NbC_{0.83}$. The appearance of this minimum is apparently due to the existence of short-range order in the arrangement of the carbon atoms and the vacancies; this could not be eliminated[75,76] even by quenching the specimens. The composition range in which the $< U_{\text{st}}^2 >$ minimum is observed corresponds to the range in which, according to the data of Refs.23 and 37, the ordered monoclinic phase Nb_6C_5 is formed on prolonged annealing.

According to Ref.65, at low concentrations of defects and in the absence of correlations in the relative positions of the atoms, the dependence of the magnitude of the mean-square static displacements on the concentration of defects c bringing about static displacements has the form:

$$\langle U_{\text{st}}^2 \rangle = c(1-c)a^2 M_0 / 2\pi^2. \qquad (11)$$

Here,

$$M_0 = R^{-1}(dV/Vdc)^2,$$

where R^{-1} is the proportionality coefficient, a the unit cell parameter, and V the unit cell volume.

In NbC_y, the defects bringing about the static distortions are structural vacancies, so that $c = (1 - y)/2$. In Ref.76 it was shown that Eqn.(11) provides a good approximation to the experimentally observed static displacements only in the composition range $0.97 < y < 1.00$ (curve *4* in Fig.6). The value of R^{-1} determined for this composition range was found to be greater by approximately two orders of magnitude than that calculated[65] for interstitial alloys of non-transition metals. This indicates that in niobium carbide the static displacements of the atoms are greater than those in the alloys, and that strong localised interactions predominate. It also follows from Fig.6 that at high concentrations of defects, the theoretical values of the displacements become much larger than the experimental values. This is apparently related to the fact that in Ref.65, in the derivation of Eqn.(11), no account was taken of the overlap of

the perturbations created by the point defects. This overlap arises in NbC_y when the deviation from stoichiometry is large, and it unavoidably leads to a decrease in the rate of increase in the static displacements with increase in the concentration of vacancies.

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The material presented shows that in the last 10–15 years the study of the local distribution of the atoms in non-stoichiometric compounds of the transition metals has developed intensively. The results of the study of the structure of non-stoichiometric compounds and their solid solutions by diffraction, resonance, and other experimental methods show that the existence of short-range order in the relative arrangement of the atoms is an extremely widespread phenomenon in these substances, whereas it was previously assumed that the distribution of the interstitial atoms in non-stoichiometric compounds was completely statistical. The study of short-range order has been particularly successful using NMR, which is highly sensitive to small changes in the symmetry of the local environment of the atoms at which resonance is observed. The study of short-range order in non-stoichiometric compounds by magnetic susceptibility, which has not previously been used for this purpose, is also noteworthy.

An analysis of the experimental data shows that the nature of the short-range order in non-stoichiometric compounds is determined chiefly by the mutual repulsion of the vacancies or atoms of the same kind. This is indicated by the negative value of the short-range order parameters for the nearest coordination spheres of the non-metal sub-lattice. Studies of short-range order in the metal sub-lattice of carbide solid solutions have detected the existence of correlations in the relative arrangement of the metal atoms, and also the influence of the carbon concentration on not only the magnitude but also the sign of the short-range order parameter for the first coordination sphere.

The breakdown of the symmetry of the local environment of the atoms in non-stoichiometric compounds leads to static displacements of both the metal atoms and the interstitial atoms. The magnitude and direction of the static displacements are different for compounds in the disordered and ordered states. Comparison of the displacements corresponding to different structural states of a compound makes it possible to analyse the nature of the inter-particle interactions. Up to the present, however, experimental work in this direction has been restricted to the study of only disordered non-stoichiometric compounds.

Thus in the last ten years, the experimental study of the local distribution of the atoms in non-stoichiometric compounds has begun, but the problem of studying short-range order in these compounds has not been resolved. This applies particularly to the ordered phases of non-stoichiometric compounds, and also to non-stoichiometric compounds synthesised under thermobaric conditions, that is with the simultaneous application of high pressures and temperatures. The preparation of ordered phases by a redistribution of the atoms in the lattice, and the thermobaric synthesis of non-stoichiometric compounds, involving the filling of structural vacancies by atoms, provide new and promising methods for the directed synthesis of substances with specified properties. Studies of short-range order and the displacements of atoms may reveal the mechanisms of the transformations taking place in non-stoichiometric compounds, the nature of the interatomic interactions, and the influence of short-range order on the properties of these compounds. The principal experimental methods which should be used as widely as possible in the study of the phenomena of short-range order in non-stoichiometric compounds are the highly sensitive pulse NMR spectroscopy, the diffuse scattering of X-rays, neutrons, and electrons, and structural neutron diffraction.

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