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## Phase transformations in non-stoichiometric vanadium carbide

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**Abstract.** X-ray diffraction, differential scanning calorimetry and reflected light microscopy studies are made of disorder–order phase transformations in the region of homogeneity of a non-stoichiometric cubic vanadium carbide,  $VC_y$  ( $0.66 < y < 0.88$ ). It is found that according to the composition of the  $VC_y$  carbide, both an ordered  $V_6C_5$  phase with monoclinic or trigonal symmetry and a cubic ordered  $V_8C_7$  phase may form in this carbide at a temperature below 1450 K. Consideration is given to the effect that non-stoichiometry and the ordering of structural vacancies have on the heat capacity of the  $VC_y$  carbide. Temperatures and heats of reversible equilibrium disorder–order transitions are determined. The ordering transformations  $VC_y$ – $V_6C_5$  and  $VC_y$ – $V_8C_7$  are shown to be first-order phase transitions. An equilibrium phase diagram of the V–C system is constructed which allows for the formation of ordered phases in a non-stoichiometric vanadium carbide. The order parameter functional method is used for calculation of phase equilibria in the region of ordering of non-stoichiometric cubic  $VC_y$  carbide.

### 1. Introduction

Vanadium forms a cubic monocarbide  $VC_y$  with  $B1$  (NaCl) structure and a lower hexagonal carbide  $V_2C_y$  ( $\beta$ - $V_2C$ ) with  $L'3$  ( $W_2C$ ) structure. These carbides possess extended regions of homogeneity, the width of which depends on temperature. For example, at 2100 K a cubic vanadium carbide  $VC_y$  and a hexagonal vanadium carbide  $V_2C_y$  display the regions of homogeneity  $VC_{0.65}$ – $VC_{0.87}$  and  $V_2C_{0.88}$ – $V_2C_{1.00}$  (or  $VC_{0.44}$ – $VC_{0.50}$ ), respectively. Vanadium carbides, alongside the carbides and nitrides of other transition metals,  $MC_y$ ,  $M_2C_y$  and  $MN_y$  ( $M = Ti, Zr, Hf, V, Nb, Ta$ ), constitute a group of strongly non-stoichiometric interstitial compounds [1, 2].

A feature peculiar to the structure of strongly non-stoichiometric  $MC_y$  and  $M_2C_y$  carbides is the intrusion of carbon atoms in the octahedral interstitial sites of the metallic sublattice; significantly, the carbon atoms may occupy only a fraction of the interstitial sites. At a sufficiently high temperature ( $>1500$  K) the carbon atoms and the unfilled interstitial sites (structural vacancies  $\square$ ) are distributed in the  $MC_y\square_{1-y}$  carbide lattice in a random fashion (statistically); in this case the probability of any non-metallic sublattice site being filled with a carbon atom coincides with the relative carbon content,  $y$ , of the  $MC_y$  carbide. Lowering the temperature leads to a redistribution of non-metallic interstitial atoms and structural vacancies and results in disorder–order phase transitions that give rise to various ordered structures (superstructures) [1–4]. Thus, the disordered state of non-stoichiometric carbides

is in thermodynamic equilibrium only at a high temperature, whereas the ordered state is in thermodynamic equilibrium at a temperature below  $\sim 1300$  K. At room temperature the disordered state of the carbides is thermodynamically non-equilibrium, but it can be readily preserved by quenching and exists as a metastable state.

As the  $VC_y$  and  $V_2C_y$  carbides undergo ordering several ordered phases are produced.

According to [5–9], a cubic ordered  $V_8C_7$  phase arises in the  $VC_y$  carbide over the range  $VC_{0.86}$ – $VC_{0.88}$ . This superstructure has a double lattice spacing with respect to the lattice spacing of a disordered carbide. The unit cell of the ordered cubic  $V_8C_7$  phase pertains to space group  $P4_332$  (or  $P4_132$ ). The other ordered phase,  $V_6C_5$ , may have trigonal (space group  $P3_1$ ) [10] or monoclinic (space group  $C2$  [11], or  $C2/m$  [12]) symmetry and was experimentally observed in vanadium carbide  $VC_y$  over the range  $0.76 \leq y \leq 0.86$ . The different unit cells of an ordered  $V_6C_5$  phase are fitted by complex diffraction data. The point is that the trigonal (space group  $P3_1$ ) superstructure and the monoclinic (space group  $C2$  and  $C2/m$ )  $M_6C_5$  superstructures are closely related; that is, they are described by close sets of superstructural wavevectors [13] and are identical in the character of short-range order [14, 15].

Near the lower boundary of the homogeneity region of the  $V_2C_y$  carbide, an ordered rhombic  $\alpha$ - $V_2C$  phase forms as a result of annealing with the temperature being slowly decreased from 1600–1800 K [16–18].

A number of papers [19–25] deal with thermodynamic characteristics of a non-stoichiometric vanadium carbide over the temperature range above 300 K. However, all these studies were made without allowance for the possibility of particular ordered structures forming in the vanadium carbide, with measurements performed with a very large temperature step. Apart from this, the poor chemical characterization of specimens and, most importantly, the absence of a trustworthy structural characterization of specimens in the papers under review do not permit one to rely on the data obtained.

Thus King [19] has used the method of drop calorimetry in the temperature range 400–1600 K to measure the enthalpy of a vanadium carbide of the expected composition  $VC_{1.00}$ , whereas the upper boundary of the homogeneity region of the vanadium monocarbide does not exceed  $VC_{0.88}$ . Using the method of mixing, Volkova and Geld [20] have investigated the enthalpy of the carbides  $VC_{0.418}O_{0.018}$ ,  $VC_{0.450}O_{0.017}$ ,  $VC_{0.508}O_{0.008}$ ,  $VC_{0.698}O_{0.006}$ ,  $VC_{0.760}O_{0.009}$ ,  $VC_{0.842}O_{0.019}$ ,  $VC_{0.861}O_{0.015}$  and  $VC_{0.884}O_{0.006}$  at temperatures from 500 to 1500 K. Relying on experimental findings [20], Tskhai *et al* [21] quote estimated data on the heat capacity of the carbides  $VC_{0.450}O_{0.017}$ ,  $VC_{0.698}O_{0.006}$ ,  $VC_{0.760}O_{0.009}$  and  $VC_{0.884}O_{0.006}$  at temperatures of 300 to 1300 K. Note that in all of the vanadium carbide specimens investigated in the temperature range 1370–1404 K, the authors of [20] observed a thermal effect (latent heat of transformation) indicative of a first-order phase transformation. The experimental error in enthalpy measurements in [20] was at least 3%, so only those thermal effects that exceed the measurement error may be viewed as reliably established. Volkova and Geld [20] have revealed such effects in the hexagonal carbide  $VC_{0.418}O_{0.018}$  and the cubic carbides  $VC_{0.760}O_{0.009}$ ,  $VC_{0.842}O_{0.019}$ ,  $VC_{0.861}O_{0.015}$  and  $VC_{0.884}O_{0.006}$ . Earlier, a similar high-temperature phase transformation was discovered in the carbide  $VC_{0.88}$  at 1393 K [22]. According to a later experimental study [23], the enthalpy of the carbides  $VC_{0.712}$ ,  $VC_{0.830}$  and  $VC_{0.861}$  in the temperature interval from 400 to 1300 K is 3–5% lower than that reported by Volkova and Geld [20]. By the method of mixing, Turtchanin *et al* [24] have determined the enthalpy of the non-stoichiometric carbides  $VC_{0.72}$ ,  $VC_{0.75}$  and  $VC_{0.86}$  over the temperature range 1300–2500 K. Korolev *et al* [25] have measured the heat capacity of six specimens of vanadium carbides with compositions between  $VC_{0.748}O_{0.008}$  and  $VC_{0.880}O_{0.004}$  on heating from 400 to 1100 K but obtained markedly high heat capacity values.

An analysis of the data reported in the literature suggests that the spread in experimental data for the heat capacity and enthalpy of non-stoichiometric vanadium carbides is large and that not a single calorimetric study is available that even mentions the structural state of the carbides investigated. Incidentally, investigations of niobium, tantalum and titanium carbides have shown that the heat capacity of a disordered carbide may differ from that of an ordered carbide of the same composition of 2–5% (see e.g. [1], [4], [26] and [27]). Let it be emphasized that still a moot point to date is whether the structural order–disorder phase transitions in the vanadium carbide are first or second order. Thus far no reliable direct evidence is available to corroborate one or the other of these viewpoints as to the nature of these phase transitions.

Thus published works on vanadium carbides furnish, on the one hand, quite good structural investigations into ordering and, on the other, thermodynamic studies made without allowance for possible disorder–order transformations and with such poor temperature resolution that the phase transitions would not have been detected.

In the present paper we make structural investigations of ordering in the vanadium carbide and perform thorough calorimetric measurements over the temperature interval 300–1600 K, where phase transformations occur that are associated with the ordering of a non-stoichiometric cubic vanadium  $VC_y$  with the basis structure  $B1$  (NaCl).

## 2. Experimental details and specimens

Specimens of non-stoichiometric vanadium carbide  $VC_y$  with various carbon contents ( $y = 0.66, 0.79, 0.83$  and  $0.87$ ) were synthesized by hot pressing of powder mixtures of metallic vanadium and vanadium carbide  $VC_{0.87}$  (vanadium carbide powder was supplied by Treibacher Powdermet, Austria). Starting powders were intensively mixed in a planetary ball mill with methanol as milling aid, dried and hot pressed in a graphite die at a temperature of about 2200 K and at a pressure of 35 MPa in high-purity argon atmosphere. The duration of hot pressing was 30 min. Layers of graphite foil and Zr foil were placed between the powder and the graphite die. The graphite foil prevented sticking between the die and the sample, which otherwise led to cracking of the samples. The Zr foil was carburized during the hot-pressing cycle and served as a getter as well as a diffusion barrier. The hot-pressed compacts were slowly cooled to room temperature within about 1 h. The initial x-ray analysis with the use of  $Cu K\alpha$  radiation showed that all the  $VC_y$  specimens produced were homogeneous and contained only one phase with a  $B1$ - (NaCl-) type crystal structure. The doublets  $K\alpha_1$  and  $K\alpha_2$  of the structure peaks  $(331)_{B1}$  and  $(420)_{B1}$  were used for determination of a base  $B1$ -type lattice period. For structure peaks the signal-to-noise ratio ranges from 70 to 100. Porosity of the compact specimens did not exceed 3%.

To produce vanadium carbide specimens in the ordered state, the compact specimens were annealed in soldered silica tubes in 0.0013 Pa vacuum; preliminarily the silica tubes were washed many times by argon. The specimens were heat treated under the following conditions: annealing at a temperature of 1200 K for 20 h, decreasing temperature down to 1100 K for 1 h, then annealing at 1100 K for 20 h, decreasing temperature to 1000 K for 1 h and finally annealing at 1000 K for 60 h followed by cooling to room temperature at a rate of  $1 K min^{-1}$ . Annealing at a temperature of 1450 K for 10 min in a soldered silica tube followed by water quenching was used to obtain disordered carbide  $VC_{0.87}$ , closely corresponding in composition to  $V_8C_7$ .

Chemical analysis of specimens for nitrogen and carbon was carried out by use of Dumas gas chromatography on a Carlo Erba CHN 1108 analyser. Free carbon was not observed in the  $VC_y$  samples. The oxygen contents of the starting powders and of the synthesized samples were measured by a vacuum hot extraction equipment Balzers exhalograph EAO-201. Note

that the phase equilibria are not affected by the minor amount (less than 0.5 wt%) of oxygen and nitrogen. The metal impurity content of the specimens as determined from the results of chemical and spectral analysis did not exceed 0.1 wt%. The chemical composition and a basic  $B1$ -type lattice period for annealed and quenched vanadium carbide  $VC_y$  specimens are given in table 1.

**Table 1.** Chemical composition and  $B1$ -type lattice period  $a_{B1}$  of non-stoichiometric annealing ordered and quenching disordered vanadium carbides  $VC_y$ .

Carbide	Chemical composition							Lattice period $a_{B1} \pm 0.00005$ (nm)	
	(wt%)				(at.%)			Ordered state	Disordered state
	C	N	O	V	C	N	O		
$VC_{0.87}$	16.94	0.09	0.31	53.1	46.1	0.21	0.64	0.41660	0.41638
$VC_{0.83}$	16.33	0.07	0.13	54.4	45.2	0.16	0.27	0.41651	0.41596
$VC_{0.79}$	15.70	0.04	0.24	55.5	43.9	0.11	0.50	0.41607	0.41548
$VC_{0.66}$	13.38	0.04	<sup>a</sup>	60.2	39.7	0.12	<sup>a</sup>	0.41305	0.41305

<sup>a</sup> Not measured.

To detect the possible ordering structures, analysis by x-ray diffraction with the use of  $Cu K\alpha$  radiation was employed. X-ray investigations were performed on powder samples at room temperature in the angular interval  $14^\circ \leq 2\theta \leq 120^\circ$  in the step scanning mode with steps of  $\Delta 2\theta = 0.02^\circ$  and an exposure time of 5 and 10 s at each point for quenched and annealed carbides, respectively.

For the metallographic analysis the samples were ground first with a diamond disc, then were polished with 3  $\mu m$  diamond paste and finally with a 1  $\mu m$  diamond suspension. For etching an aqueous solution 10% KOH + 10%  $K_3[Fe(CN)_6]$  was used (concentration is given in wt%). After polishing and etching, microstructures of annealed compact specimens were investigated in polarized reflected white light.

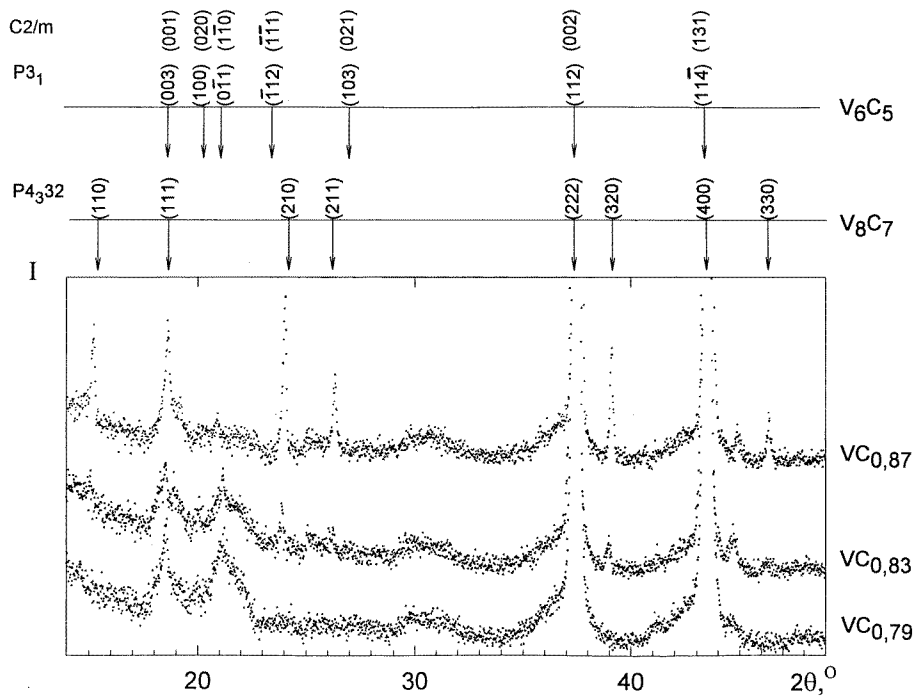
Thermodynamic properties of vanadium carbide were determined with a Netzsch 404 (Germany) differential scanning calorimeter between 300 and 1600 K in inert atmosphere of highly pure argon. Measurements were made at a heating and cooling rate of 20 K  $min^{-1}$ . The samples had the form of a disc of 5 mm in diameter and 1 mm thick. To accurately measure the heats of transition in the vanadium carbide, prior calibration experiments were performed under the same conditions on specimens with known melting temperatures. For calibration in the temperature range 900–1600 K, we used high-purity aluminium Al and gold Au with melting temperatures of 933 and 1336 K, respectively. Sapphire and gold standards were used as reference materials. The accuracy of the heat capacity measurements at a given temperature was about 1%. The relative mean error in phase transformation heat did not exceed 5%.

### 3. Results and discussion

As a result of the annealing of non-stoichiometric vanadium carbide specimens under the conditions described in section 2, the x-ray diffraction patterns of  $VC_{0.79}$ ,  $VC_{0.83}$  and  $VC_{0.87}$  specimens exhibited extra peaks alongside intense lattice reflections. The intensity of extra peaks was never more than 5% of the intensity of average structure peaks. The appearance of additional low-intensity reflections testifies to ordered phases forming in the heat-treated specimens. With the vanadium carbide  $VC_{0.66}$  subjected to heat treatment, the x-ray pattern exhibited no extra reflections.

## 3.1. Crystal structure

In figure 1 we show fragments of x-ray diffraction patterns for annealed  $VC_{0.79}$ ,  $VC_{0.83}$  and  $VC_{0.87}$  specimens. The intense lines exhibited by all the x-ray diffraction patterns in the range of angles  $2\theta = 37.4$  and  $43.4^\circ$  are lattice reflections  $(111)_{B1}$  and  $(200)_{B1}$ . The x-ray diffraction patterns of all the annealed carbides display in the region of angles  $2\theta \approx 21.2$ – $22.0^\circ$  and  $\sim 30.0$ – $31.0^\circ$  weak and broad maxima, which are absent from the x-ray pictures of disordered carbides. There are some possible reasons for the occurrence of these diffuse peaks. Observed diffuse maxima can be connected with double Bragg scattering. However the vanadium carbide powder used is fine grained (the grain size less than  $1 \mu\text{m}$ ); therefore it is impossible to accept such an explanation synonymously. Besides, double Bragg scattering is usually observed in the region of low angles  $2\theta < 10^\circ$ . The second possible reason is that these maxima are spurious reflections from wavelength  $\lambda/2$  radiation and correspond to structural reflections  $(200)_{B1}$  and  $(220)_{B1}$ . They arise from the large accumulation as x-ray diffraction patterns of annealed carbides are taken. Third, the most probable reason is the presence of short-range order in annealed vanadium carbide samples. It is necessary to perform more detailed investigations of the low-angle scattering for a reliable explanation of the diffuse maxima observed. In addition, all the x-ray diffraction patterns show in the range of angles  $2\theta \approx 44.5$ – $45.0^\circ$  an extrinsic line, which we have not been able to identify.



**Figure 1.** X-ray diffraction patterns of annealing non-stoichiometric vanadium carbides  $VC_{0.87}$ ,  $VC_{0.83}$  and  $VC_{0.79}$ . The arrows show the position of the superstructural reflections corresponding to the  $V_6C_5$  and  $V_8C_7$  ordered phases; the Miller indices corresponding to the space group of the ordered phase are given for all reflections.

In the x-ray diffraction pattern of an annealed  $VC_{0.87}$  carbide, the first superstructure reflection with the diffraction vector  $|\mathbf{q}| = (2a_{B1} \sin \theta)/\lambda \approx 0.710$  is observed for the angle

$2\theta = 15.14^\circ$  (figure 1). This reflection corresponds to the superstructural vector  $\{1/2\ 1/2\ 0\}$ , which has a length  $|\mathbf{q}| \approx 0.707$  and pertains to star  $\{\mathbf{k}_4\}$  with a running index  $\mu_4 = 1/4$  (here and henceforth the notation of the wavevector stars  $\{\mathbf{k}_s\}$  belonging to the first Brillouin zone of an FCC crystal as well as the notation of their arms  $\mathbf{k}_s^{(j)}$  is given according to [1] and [28], which provide a detailed description of all the stars). The next reflection with  $|\mathbf{q}| \approx 0.871$  is observed at  $2\theta = 18.55^\circ$  and corresponds to the vector  $\{1/2\ 1/2\ 1/2\}$  of star  $\{\mathbf{k}_9\}$ . Of all the superstructural peaks, it is the third reflection ( $2\theta = 24.04^\circ$ ) that has the highest intensity. This peak corresponds to the vector  $\{1\ 1/2\ 0\}$  of star  $\{\mathbf{k}_5\}$ . The further three superstructural peaks presented in the x-ray diffraction pattern of an annealed VC<sub>0.87</sub> carbide (figure 1) are observed at angles  $2\theta = 26.34^\circ$ ,  $39.14^\circ$  and  $46.34^\circ$  and correspond to the vector  $\{1\ 1/2\ 1/2\}$  of star  $\{\mathbf{k}_4\}$ , to the vector  $\{3/2\ 1\ 0\}$  of star  $\{\mathbf{k}_8\}$  and to the vector  $\{3/2\ 3/2\ 0\}$  of star  $\{\mathbf{k}_4\}$ . In the range of angles  $2\theta$  between  $14^\circ$  and  $110^\circ$ , a total of 19 superstructural reflections are observed in the diffraction spectrum of an annealed VC<sub>0.87</sub> carbide, which corresponds to three stars, viz.,  $\{\mathbf{k}_9\}$ ,  $\{\mathbf{k}_8\}$  and  $\{\mathbf{k}_4\}$ .

A metallographic analysis of an annealed VC<sub>0.87</sub> carbide has confirmed the presence in it of an ordered phase that belongs to the cubic crystal system. After etching, microsection metallographic specimens exhibit distinct ordered-phase domains isometric in shape. In reflected polarized white light, ordered phases cause no interference; this provides clear evidence of the ordered V<sub>8</sub>C<sub>7</sub> phase being isotropic. Microstructural investigations have shown that the disorder–order phase transformation in the VC<sub>0.87</sub> carbide begins at the grain boundaries of the disordered carbide and with time spreads deep into the crystallites.

An analysis of the position and intensity of the superstructure reflections observed shows that heat treating the VC<sub>0.87</sub> has given rise to a cubic ordered V<sub>8</sub>C<sub>7</sub> phase. The unit cell of the ordered V<sub>8</sub>C<sub>7</sub> phase has a double lattice spacing compared with the spacing compared with the spacing of the basis structure of the ordered phase. The channel of the disorder–order structural phase transition VC<sub>0.87</sub>  $\rightarrow$  V<sub>8</sub>C<sub>7</sub> incorporates all arms of the Lifschitz stars  $\{\mathbf{k}_9\}$  and  $\{\mathbf{k}_8\}$  and of the non-Lifschitz star  $\{\mathbf{k}_4\}$  (with  $\mu_4 = 1/4$ ). The superstructure wavevectors do not satisfy the Landau group-theoretical criteria for possible second-order phase transitions, and hence the transition is necessarily discontinuous. Thus, even from symmetry considerations, it is clear that the formation of an ordered V<sub>8</sub>C<sub>7</sub> phase can occur only as a first-order transition. This is in agreement with theoretical conclusions [29].

An analysis of the x-ray diffraction pattern of an annealed VC<sub>0.83</sub> carbide (figure 1) has shown this specimen to contain two ordered phases. Along with the superstructural reflections that correspond to an ordered V<sub>8</sub>C<sub>7</sub> phase, there are also lines from an ordered V<sub>6</sub>C<sub>5</sub> phase with trigonal or monoclinic symmetry. The first reflection is observed for the angle  $2\theta = 18.54^\circ$  and is indexed as  $\{1/2\ 1/2\ 1/2\}$ . This reflection corresponds to an ordered V<sub>6</sub>C<sub>5</sub> phase and is the arm  $\mathbf{k}_9^{(1)}$  of the star  $\{\mathbf{k}_9\}$ . The reflections  $2\theta = 20.11^\circ$   $\{2/3\ 2/3\ 0\}$ ,  $2\theta = 21.14^\circ$   $\{1/6\ -5/6\ -1/2\}$ ,  $2\theta = 23.74^\circ$   $\{-1/3\ -1/3\ 1\}$  and  $2\theta = 27.34^\circ$   $\{7/6\ 1/6\ 1/2\}$ , which correspond to the stars  $\{\mathbf{k}_4\}$  (with  $\mu_4 = 1/3$ ) and  $\{\mathbf{k}_3\}$  (with  $\mu_3 = 1/6$ ), belong to an ordered V<sub>6</sub>C<sub>5</sub> phase too. Therefore, the disorder–order phase transition channel associated with the formation of the V<sub>6</sub>C<sub>5</sub> superstructure comprises the arms of the Lifschitz star  $\{\mathbf{k}_9\}$  and of the non-Lifschitz stars  $\{\mathbf{k}_4\}$  and  $\{\mathbf{k}_3\}$ . From symmetry considerations, it is clear that the formation of an ordered V<sub>6</sub>C<sub>5</sub> phase should proceed as a first-order phase transition.

The totality of the observed superstructural wavevectors forming the VC<sub>0.83</sub>  $\rightarrow$  V<sub>6</sub>C<sub>5</sub> transition channel may correspond to a trigonal (space group  $P3_1$ ) or a monoclinic (space group  $C2/m$ ) M<sub>6</sub>C<sub>5</sub>-type superstructure. Earlier [29], the powder diffraction patterns of these ideal superstructures were shown to be very similar in the position and intensity of superstructural reflections. For real ordered M<sub>6</sub>C<sub>5</sub> phases (space groups  $P3_1$  and  $C2/m$ ), the intensities of the superstructural reflections are slightly different owing to a difference in the directions and

magnitude of static atomic displacements. Results of an analysis of the diffraction spectrum of the  $V_6C_5$  superstructure with allowance for possible static shifts of atoms will be presented as a separate publication.

A study of the microstructure of an annealed  $VC_{0.83}$  carbide in reflected polarized white light has shown the specimen to contain domains of two ordered phases. The grains of one of the phases are predominantly isometric in shape and produce no interference colours, i.e. this ordered phase is isotropic, and may therefore be viewed as a cubic ordered  $V_8C_7$  phase. It is present in the specimen to the extent of 15–20%. The second phase in the specimen accounts for 80–85%. The domains of the second phase have a tabular and prismatic shape and possess interference colours, i.e. are anisotropic. Typical microstructures observed with reflected polarized white light contain blue and yellow regions corresponding to ordered domains of the second phase. All this permits the second phase to be viewed as a  $V_6C_5$  phase. Thus, the results of the investigation of the microstructure fit well with the conclusions drawn from diffraction data.

The x-ray diffraction pattern of an annealed  $VC_{0.79}$  carbide exhibits superstructural reflections that belong to only an ordered  $V_6C_5$ -type structure (figure 1). The microstructure of the annealed  $VC_{0.79}$  carbide contains domains of only an anisotropic ordered phase. Therefore, protracted annealing has resulted in a single  $V_6C_5$ -type phase forming carbide  $VC_{0.79}$ .

The x-ray diffraction pattern of the  $VC_{0.66}$  carbide after annealing showed only structural reflections from a cubic phase with  $B1$  (NaCl) structure; no extra reflections had appeared although a rhombic  $\zeta$ - $V_4C_{3-x}$  phase could be expected to arise in this carbide. For the first time the  $\zeta$ - $M_4C_{3-x}$  carbide was detected in the Ta–C [30] and Nb–C [31] systems and described as a metastable phase of composition  $M_3C_2$ . Indeed,  $\zeta$ - $M_4C_{3-x}$  ( $x \leq 0.33$ ) carbides have a defective carbon sublattice and formally (without taking into account the crystal structure) coincide in composition with  $M_3C_2$  ( $MC_{0.67}$ ). Thus far it has not been possible to isolate  $\zeta$ - $V_4C_{3-x}$  as an independent phase: this carbide occurs only in the presence of other phases, to the extent of no more than 15–20%. The  $\zeta$ - $V_4C_{3-x}$  carbide is not an ordered phase of the cubic  $VC_y$  carbide as it has rhombic rather than an FCC metallic sublattice [32]. according to [33],  $\zeta$ - $V_4C_{3-x}$  forms and is stable at a temperature below 1593 K. The absence of the  $\zeta$ - $V_4C_{3-x}$  phase in an annealed  $VC_{0.66}$  carbide is due apparently to the fact that the annealing was performed from a lower temperature, namely 1200 K. Note that in composition the  $VC_{0.66}$  carbide corresponds to the lower boundary of the homogeneity region of the  $\zeta$ - $V_4C_{3-x}$  phase.

### 3.2. Period of a basic $B1$ -type lattice

A disordered phase with a  $B1$ -type structure, which is a base for the formation of ordered phases, is called a basic phase. A period of a  $B1$ -type crystal lattice is called a basic  $B1$ -type lattice period. Structural reflections corresponding to a  $B1$ -type crystal structure also exist in diffraction patterns of ordered phases, therefore a basic  $B1$ -type lattice period can be derived for ordered phases.

Measurements showed that a basic  $B1$ -type lattice period of ordered vanadium carbide is greater than that for the quenched disordered carbide  $VC_y$  of the same composition. A similar effect was observed previously in titanium [34], niobium [1, 35] and tantalum [36] carbides. The effect of heat treatment conditions on the lattice period of the  $VC_{0.74}$  carbide was discovered by Storms and McNeal [37]: the  $VC_{0.74}$  carbide when quenched from 1700 K had the lattice period  $a_{B1} = 0.4125 \pm 0.0001$  nm; the same carbide annealed with a slow decrease in temperature from 1620 K had the period  $a_{B1} = 0.4131 \pm 0.0001$  nm. The authors of [37] were not able to provide an explanation for this effect.

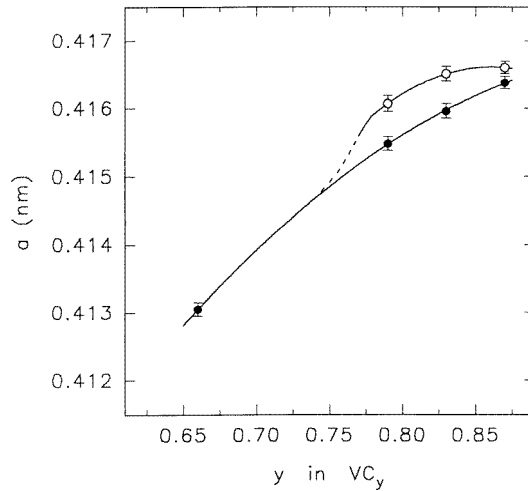


Later, a lattice period increase was observed at the  $\text{VC}_{0.89} \rightarrow \text{V}_8\text{C}_7$  disorder–order transition in a vanadium carbide [38]. At room temperature the base lattice period of quenched disordered carbide  $\text{VC}_{0.89}$  was 0.41662 nm, whereas in the ordered carbide of the same composition it was 0.41667 nm (i.e., 0.83334 nm for the cubic superstructure  $\text{V}_8\text{C}_7$ , whose lattice period is twice that for the basic lattice). This compares favourably with high-temperature x-ray results which show a sudden change from 0.4202 to 0.4200 nm in a basic lattice period of vanadium carbide at the  $\text{V}_8\text{C}_7 \rightarrow \text{VC}_{0.89}$  order–disorder transition at  $T = 1413 \pm 10$  K.

Figure 2 shows the variation with carbon content of the basic lattice period of disordered and ordered vanadium carbide  $\text{VC}_y$ . An increasing vacancy concentration is accompanied by a nonlinear decreasing lattice period  $a_{B1}$  of  $\text{VC}_y$ . The data on the lattice period of a disordered ( $\eta = 0$ ) vanadium carbide  $\text{VC}_y$  were approximated by a second-order polynomial

$$a(y, 0) = a_0 + a_1y + a_2y^2 \quad (1)$$

with  $a_0 = 0.38285$ ,  $a_1 = 0.06899$  and  $a_2 = -0.03475$  nm.



**Figure 2.** The dependence of the period of a basic *B1*-type crystal lattice on the composition of a disordered (●) and ordered (○) vanadium carbide  $\text{VC}_y$ .

Experimentally, the appearance of structural vacancies in disordered carbide is evident from the reduction in lattice period  $a_{B1}$  whereas ordering is accompanied by an increase in the basic lattice period  $a_{B1}$  of the carbide. Ordering is observed at a comparatively high vacancy concentration ( $0.21 \leq 1 - y \leq 0.21$ ). In a disordered carbide at such concentration the vacancy perturbation regions overlap and partially compensate one another. In an ordered carbide nearest-neighbour structural vacancies are absent, so this overlap is significantly less than in a disordered carbide. It is easily understood that a basic lattice period increase is only possible when metallic atoms move away from the vacancy. In contrast, if they move toward it, the basic lattice period of an ordered carbide should be less than that of a disordered carbide.

Thus an increase in the basic lattice period of an ordered carbide compared with a disordered carbide and a reduction in the lattice period with increasing vacancy concentration are possible when two conditions are realized simultaneously: (i) if the atoms forming the first coordination sphere of the vacancy move away from the vacancy and (ii) if the crystal lattice perturbations due to the vacancy extend over no fewer than two coordination spheres.

This is consistent with the experimental data on the static displacements of metal atoms: in non-stoichiometric titanium, zirconium and niobium carbides the metal atoms of the first coordination sphere move away from the vacancy [39, 40]; according to [41], in  $NbC_y$  the niobium atoms in the first coordination sphere move away from the vacancy and those in the second sphere move towards the vacancy.

Let us consider a phenomenological model to analyse the increase in lattice period at ordering of non-stoichiometric  $MC_y$  carbide. Earlier [36, 42], this model was proposed for analysing changes in lattice spacing as ordered phases of only one type,  $M_6C_5$ , form in the  $NbC_y$  and  $NaC_y$  carbides. We wish to discuss its application to the various ordered  $M_{2t}C_{2t-1}$  phases ( $t = 1, 1.5, 2, 3$  and  $4$ ) that may form in highly non-stoichiometric carbides.

In non-stoichiometric carbides with a base  $B1$ - ( $NaCl$ -) type structure, each metal atom has an environment of six non-metallic sublattice sites which can either be occupied by carbon atoms or be vacant. This allows us to represent non-stoichiometric carbide  $MC_y$  with  $B1$ -type structure as a set of clusters in the form of the Dirichlet–Voronoi polyhedron, a distorted Wigner–Seitz cell. Each cluster is the rhombic dodecahedron and contains a metal atom and six non-metallic sublattice sites. Note that each non-metallic sublattice site belongs to six neighbouring polyhedra simultaneously. Such clusters fill the entire volume of the crystal and account for all the lattice sites.

In the first approximation let us assume that the cluster volume  $V_m$  depends only on the number of vacancies,  $m$ , in it and is independent of their mutual arrangement. In this case the crystal volume  $V$  may be represented as

$$V = N \sum_{m=0}^6 \lambda_m P_m(y, \eta) V_m \quad (2)$$

where  $P_m(y, \eta)$  is the probability that a cluster with a number of vacancies equal to  $m$  occurs in the crystal,  $\eta$  is the long-range order parameter,  $\lambda_m = C_6^m$  is the multiplicity of the  $m$ -configuration of the cluster (the symbol  $C_6^m$  stands for the number of permutations of  $m$  out of 6) and  $N$  is the total number of metallic sublattice sites. On other hand, the crystal volume may be written in terms of the basic period,  $a_{B1}(y)$ , as  $V = (N/4)a^3(y)$ . Allowing for this and equations (1) and (2), we obtain for a disordered carbide

$$\sum_{m=0}^6 \lambda_m P_m(y, 0) V_m = \frac{(a_0 + a_1 y + a_2 y^2)^3}{4} \quad (3)$$

where  $P_m(y, 0) = (1 - y)^m y^{(6-m)}$  is the probability of formation of a cluster with  $m$  vacancies in a disordered carbide. The solution to equation (3) is an expression for cluster volume  $V_m$ :

$$V_m = \frac{1}{4} \sum_{k=m}^6 A_{6-k} \frac{k!(6-m)!}{6!(k-m)!} \quad (4)$$

with  $A_{6-k}$  are the coefficients of  $y^k$  on the right-hand side of equation (3).

A contribution of each cluster to the total crystal volume is proportional to probability  $P_m$ . For equilibrium conditions, the probability  $P_m(y, \eta)$  that a cluster with  $m$  vacancies exists in the ordered  $M_{2t}C_{2t-1}$  phase with any degree of long-range order [1, 4, 43] has the form (5)

$$P_{m,t}(y, \eta) = \frac{1}{\Phi} \sum_f \frac{g_f}{C_6^{v(t,f)}} \sum_{v=0}^{v(t,f)} C_{6-m}^{v(t,f)-v} C_m^v n_1^{[v(t,f)-v]} n_2^{[6-m-v(t,f)+v]} (1 - n_1)^v (1 - n_2)^{(m-v)} \quad (5)$$

where  $n_1 = y - (2t - 1)\eta/2t$  and  $n_2 = y + \eta/2t$  are the probabilities of finding a carbon atom on a vacancy sublattice site or on a carbon sublattice site, respectively, as the  $M_{2t}C_{2t-1}$ -type

superstructure is forming;  $g_f$  is the multiplicity of the non-equivalent position of the metal atom which is a centre of each cluster ( $\sum_f g_f = \Phi$ );  $v(t, f)$  is the number of vacancy sublattice sites, which belongs to the cluster with multiplicity  $g_f$  in the  $M_{2t}C_{2t-1}$ -type superstructure.

Using equations (2), (4) and (5), one can find the crystal volume and hence the period of a basic  $B1$ -type lattice for non-stoichiometric carbide with any degree of order. Calculation of the basic lattice period of ordered vanadium carbide was carried out in two ways.

In the first approach it was assumed that the maximum possible degree of long-range order,  $\eta_{\max}$ , in vanadium carbide is achieved. According to [1] and [4] the dependence of  $\eta_{\max}$  on the composition of  $MC_y$  carbide during the formation of an ordered  $M_{2t}C_{2t-1}$  type phase has the form

$$\eta_{\max}(y) = \begin{cases} 2t(1-y) & \text{if } y \geq (2t-1)/2t \\ 2ty/(2t-1) & \text{if } y < (2t-1)/2t. \end{cases} \quad (6)$$

For  $VC_{0.79}$ ,  $VC_{0.83}$  and  $VC_{0.87}$  carbides  $\eta_{\max}$  is equal to 0.948, 1.0 and 0.994, respectively.

In the second approach it was assumed that in ordered vanadium carbide the long-range order parameter has the same value as at the disorder–order transition temperature  $T_{\text{trans}}$ , i.e.  $\eta = \eta_{\text{trans}}$ . The  $\eta_{\text{trans}}$  values for the disorder–order  $MC_y \rightarrow M_6C_5$  and  $MC_y \rightarrow M_8C_7$  transitions are given in [4]. For  $VC_{0.79}$ ,  $VC_{0.83}$  and  $VC_{0.87}$  carbides  $\eta_{\text{trans}}$  is equal to 0.612, 0.635 and 0.720, respectively.

Comparison of the experimental and calculated  $\Delta a = a(y, \eta) - a(y, 0)$  values (table 2) shows that in a case of  $VC_y$ – $V_6C_5$  transformation experimental data is almost exactly average between the two theoretical values. For  $VC_{0.87}$  carbide the value of  $\Delta a$  obtained in the  $\eta = \eta_{\text{trans}}$  approximation is nearest to the experimental value. Thus, ordered phases of vanadium carbide  $VC_y$  have the degree of long-range order that is nearest to the thermodynamically equilibrium distribution of carbon atoms and structural vacancies in the crystal lattice. Note that the change in the lattice period of vanadium carbide  $VC_y$  during ordering is comparable with lattice period change within that part of the homogeneity region of  $VC_y$  where ordered phases form. In the region  $VC_{0.79}$ – $VC_{0.83}$ , the change in lattice period is 0.00048 nm, whereas maximum ordering-induced change is equal to 0.00059 nm. Thus, effects of non-stoichiometry and ordering on a basic lattice period of  $VC_y$  are comparable in magnitude.

**Table 2.** Change  $\Delta a = a(y, \eta) - a(y, 0)$  in a base  $B1$ -type lattice period, during ordering of non-stoichiometric vanadium carbide  $VC_y$ .

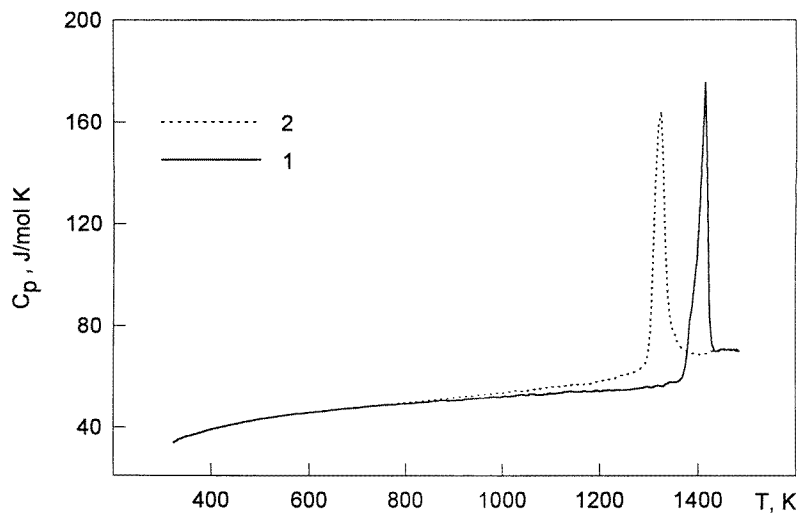
Carbide		$\Delta a = a(y, \eta) - a(y, 0)$ (nm)		
		Experimental	Calculation	
Phase transformation	$\pm 0.000\ 10$		$\eta = \eta_{\text{trans}}$	$\eta = \eta_{\max}$
$VC_{0.66}$	—	0	—	—
$VC_{0.79}$	$VC_y \rightarrow V_6C_5$	0.000 59	0.000 31	0.000 79
$VC_{0.63}$	$VC_y \rightarrow V_6C_5$	0.000 55	0.000 33	0.000 86
$VC_{0.87}$	$VC_y \rightarrow V_8C_7$	0.000 22	0.000 27	0.000 47

### 3.3. Heat capacity

Heat capacity measurements for annealed vanadium carbide specimens were performed when heating the specimens from 300 to 1500–1600 K, and in subsequent cooling from the highest heating temperature to room temperature. The heat capacity versus temperature

curve,  $C_p(T)$ , showed the occurrence of the order–disorder transition on both heating and cooling. The transition temperature was displaced upwards from equilibrium temperature on the heating cycle, and displaced below the equilibrium temperature on the cooling cycle.

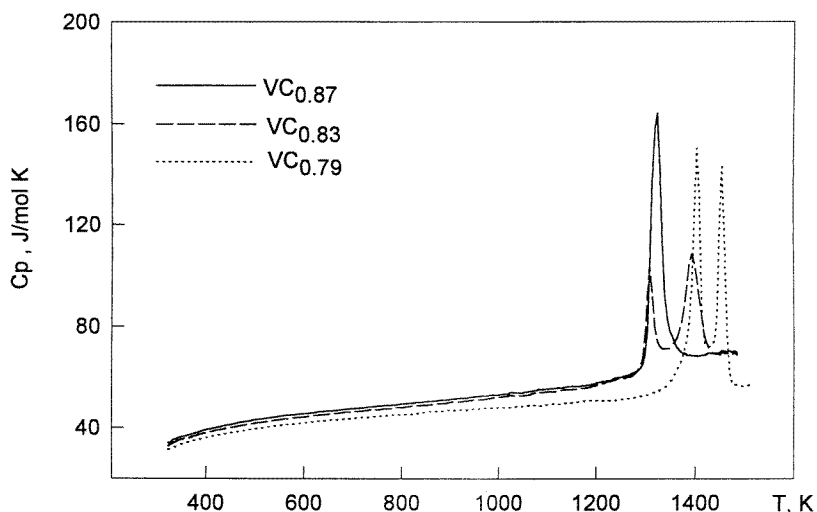
Measurements of the heat capacity,  $C_p$ , of an annealed  $VC_{0.87}$  carbide reveal that as the temperature is raised from 300 to 1350 K the quantity  $C_p$  increases gradually owing to the excitation of the phonon subsystem. Then a dramatic heat capacity jump (discontinuity) takes place at temperature  $\sim 1380$  K (figure 3), which comes from the  $V_8C_7 \rightarrow VC_y$  order–disorder transformation. Note that the heat capacity spike is typical of almost any order–disorder transformation, but the symmetrical shape rather than  $\lambda$ -curve is more typical of first-order than second-order phase transitions. On cooling from 1500 K, a similar situation arises, with the only difference that the heat capacity peak due to the disorder–order phase transition is shifted towards lower temperatures (figure 3). The temperature interval between forward-trend and reverse-trend heat capacity peaks represents a region of metastability, the presence of which is a further indication that the reversible disorder–order phase transition associated with the formation of an ordered  $V_8C_7$  phase is first order. Note that in the vicinity of the transition temperature,  $T_{trans}$ , the heat capacity of a disordered carbide is appreciably higher than that of an ordered carbide. Similar heat capacity behaviour on order–disorder transition was theoretically predicted for non-stoichiometric  $MC_y$  carbides by Gusev *et al* [44, 45]. The observation of only one heat capacity peak for  $VC_{0.87}$  carbide is consistent with the occurrence of only one phase transformation, and the observation of only cubic ordered  $V_8C_7$  phase in the annealed  $VC_{0.87}$  carbide (see section 3.1).



**Figure 3.** Heat capacity  $C_p$  of annealing vanadium carbide  $VC_{0.87}$  of heating (1) and cooling (2).

Heat capacity–temperature curves for the vanadium carbides  $VC_{0.83}$ ,  $VC_{0.79}$  and  $VC_{0.87}$  as measured with cooling from 1500 K are given in figure 4. As can be seen, by contrast with the  $VC_{0.87}$  carbide, the  $C_p(T)$  curves of  $VC_{0.79}$  and  $VC_{0.83}$  have two peaks.

With a disordered  $VC_{0.83}$  carbide being cooled from 1500 K over the range 1440–1400 K, a first heat capacity jump occurs; as the temperature is lowered further in the interval 1330–1300 K the  $C_p(T)$  curve exhibits a second peak (figure 4). In carbon content, the  $VC_{0.83}$



**Figure 4.** A comparison of phase transformation effects observed in the heat capacity–temperature curves,  $C_p(T)$ , for  $VC_{0.87}$ ,  $VC_{0.83}$  and  $VC_{0.79}$  carbides when cooled from 1500 K.

carbide corresponds to the stoichiometric composition of an ordered  $V_6C_5$  phase, so it may be assumed that the first heat capacity jump at 1400–1440 K stems from the  $VC_{0.83} \rightarrow V_6C_5$  transition. The successive transformation that takes place at a temperature of 1330 K may be associated with an ordered  $V_8C_7$  phase forming by the solid-phase transformation  $VC_{0.83} + V_6C_5 \rightarrow V_6C_5 + V_8C_7$ . Support for this comes from the fact that the x-ray diffraction pattern of an annealed  $VC_{0.83}$  carbide exhibits superstructural lines that belong not only to the  $V_6C_5$  phase, but also to the cubic ordered  $V_8C_7$  phase (figure 1). This means that the region of existence of an ordered  $V_8C_7$  phase in the vanadium carbide  $VC_y$  extends to at least the composition  $VC_{0.83}$ .

When an annealed  $VC_{0.79}$  carbide is subjected to heating, the temperature dependence of heat capacity exhibits two peaks as well, at  $\sim 1440$  K and  $\sim 1475$  K. With the specimen cooled from 1500 K, both peaks persist in the  $C_p(T)$  curve, but the high-temperature peak increases slightly in intensity (figure 4). The low-temperature peak in the  $C_p(T)$  curve of the  $VC_{0.79}$  carbide almost coincides in position with the high-temperature peak in the  $C_p(T)$  curve for the  $VC_{0.83}$  carbide and may therefore be assumed to arise from the reversible disorder–order transition,  $V_6C_5 \leftrightarrow VC_y$ . This is consistent with structural data: the x-ray diffraction pattern of an annealed  $VC_{0.79}$  shows superstructural reflections from only an ordered  $V_6C_5$  phase (figure 1).

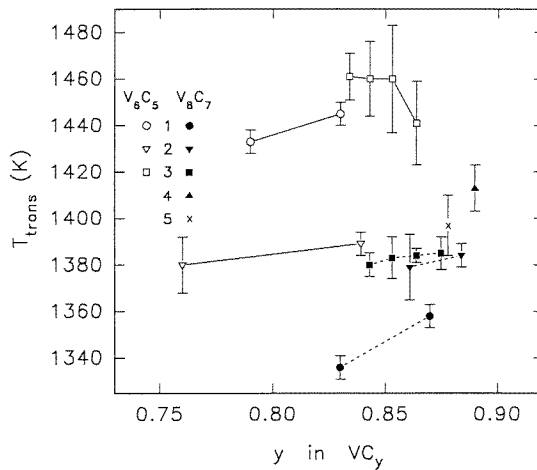
The high-temperature peak in the  $C_p(T)$  curve of the  $VC_{0.79}$  carbide comes apparently from the rhombic  $\zeta$ - $V_4C_{3-x}$  phase of the vanadium carbide. The  $\zeta$ - $V_4C_{3-x}$  carbide is observed only in the presence of other phases, to the extent of no more than 15–20%, and forms, according to [33], at a temperature below 1593 K. In carbon content, the  $VC_{0.79}$  carbide corresponds to the upper boundary of the homogeneity region of the  $\zeta$ - $V_4C_{3-x}$  phase, so it may contain only a small amount (under 3–5%)  $\zeta$ -phase. Allowing for the foregoing, the sequence of phase transformations in the  $VC_{0.79}$  carbide boils down to what follows.

In the measurement of heat capacity, slowly heating the  $VC_{0.79}$  carbide to  $\sim 1400$  K gives rise to an ordered  $V_6C_5$  phase forming in it and leads to formation of a small amount (less than 5%) of  $\zeta$ - $V_4C_{3-x}$  phase that is hard to detect by x-ray phase analysis. As the  $VC_{0.79}$  carbide is

heated further, a  $V_6C_5 \rightarrow VC_y$  order–disorder transition takes place at a temperature of about 1440 K whereas at  $\sim 1480$  K the  $\zeta$ - $V_4C_{3-x}$  carbides breaks down, i.e. a  $\zeta$ - $V_4C_{3-x} \rightarrow VC_y$  transformation occurs. When the specimen is cooled from 1500 K some amount of  $\zeta$ - $V_4C_{3-x}$  forms initially; further lowering the temperature leads to ordering of the  $VC_{0.79}$  carbide and to forming of a  $V_6C_5$  phase.

Table 3 presents the temperatures  $T_{\text{trans}}$  and heats  $\Delta H_{\text{trans}}$  of the phase transformations observed experimentally in the  $C_p(T)$  curves of the vanadium carbides  $VC_{0.79}$ ,  $VC_{0.83}$  and  $VC_{0.87}$ . Inspection of table 3 shows that the highest temperatures  $T_{\text{trans}}$  of the  $V_6C_5 \leftrightarrow VC_y$  and  $V_8C_7 \leftrightarrow VC_y$  transitions are exhibited by the  $VC_{0.83}$  and  $VC_{0.87}$  carbides that correspond to the stoichiometric compositions of ordered phases. The temperatures  $T_{\text{trans}}$  of the  $V_6C_5 \leftrightarrow VC_y$  transitions are  $\sim 90$  K higher than the counterparts of the  $V_8C_7 \leftrightarrow VC_y$  transitions.

Shown in figure 5 are data on the  $T_{\text{trans}}$  of the  $V_6C_5 \leftrightarrow VC_y$  and  $V_8C_7 \leftrightarrow VC_y$  transitions as obtained by us and the other authors [20, 31, 46, 47]. The values of temperatures  $T_{\text{trans}}$  that we have measured are approximately 20–25 K lower than those reported by Emmons and Williams [46]; allowing for the measurement errors for  $T_{\text{trans}}$ , which amount to  $\pm 5$  K in the present paper and to  $\pm 15$  K in [46], the fit may be considered fairly good. The results of Volkova and Geld [20] for the  $V_6C_5 \leftrightarrow VC_y$  transition temperature  $T_{\text{trans}}$  are obviously underestimates, while the value  $T_{\text{trans}} = 1548 \pm 10$  K given for the same transition by Shaklette and Williams [47] is highly overstated. According to our results and the data of [20], [46] and [47], the value of  $T_{\text{trans}}$  for the  $V_8C_7 \leftrightarrow VC_{0.87-0.88}$  transition ranges between 1358 and 1397 K (figure 5). Athanassiadis *et al* [38] report  $T_{\text{trans}} = 1413$  K, apparently an overestimate. It may be assumed that the most probable value of  $T_{\text{trans}}$  for the  $V_8C_7 \leftrightarrow VC_{0.875}$  transition should be equal to 1380 K.



**Figure 5.** Transition temperatures  $T_{\text{trans}}$  for the  $V_6C_5 \leftrightarrow VC_y$  and  $V_8C_7 \leftrightarrow VC_y$  phase transformations as a function of carbon content  $y$  in vanadium carbide  $VC_y$ : 1, present paper; 2, from [20]; 3, from [46]; 4, from [38]; 5, from [47].

The measured heats of ordering-type phase transformations in the  $VC_y$  carbide (table 3) are close enough to results reported in the literature. According to [46], the heats  $\Delta H_{\text{trans}}$  of the  $V_6C_5 \leftrightarrow VC_{0.833}$  and  $V_8C_7 \leftrightarrow VC_{0.875}$  transitions are equal to  $1.45 \pm 0.71$  and  $1.54 \pm 0.62$   $\text{kJ mol}^{-1}$  respectively; according to [20], the heats of phase transformations in the  $VC_{0.842}$  and  $VC_{0.844}$  carbides are 2.38 and 2.06  $\text{kJ mol}^{-1}$ .

**Table 3.** Experimental phase transformation temperatures  $T_{\text{trans}}$  and heats  $\Delta H_{\text{trans}}$  in non-stoichiometric vanadium carbide  $\text{VC}_y$ .

Carbide $\text{VC}_y$	Phase transformation											
	$\text{V}_6\text{C}_5 \leftrightarrow \text{VC}_y$				$\text{V}_8\text{C}_7 \leftrightarrow \text{VC}_y$				$\zeta\text{-V}_4\text{C}_{3-x} \leftrightarrow \text{VC}_y$			
	$T_{\text{trans}} \pm 5$ (K)	Heating	Cooling	$\Delta H_{\text{trans}}$ (kJ mol <sup>-1</sup> )	$T_{\text{trans}} \pm 5$ (K)	Heating	Cooling	$\Delta H_{\text{trans}}$ (kJ mol <sup>-1</sup> )	$T_{\text{trans}} \pm 5$ (K)	Heating	Cooling	$\Delta H_{\text{trans}}$ (kJ mol <sup>-1</sup> )
$\text{VC}_{0.79}$	1433	1428	2.11	-2.22	—	—	—	—	1473	1473	1.56	-1.64
$\text{VC}_{0.83}$	1445	1438	1.16	-1.37	1336	1331	0.64	-0.75	—	—	—	—
$\text{VC}_{0.87}$	—	—	—	—	1358	1353	2.23	-2.35	—	—	—	—

Experimental data for the heat capacity of ordered VC<sub>y</sub> carbides with different carbon content over the range between 298 and 1300 K were approximated by the following equations.

$$\text{VC}_{0.79}: C_p(T) = 61.26 - 0.0136T + 8.479 \times 10^{-6}T^2 - 8437T^{-1} \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (7a)$$

$$\text{VC}_{0.83}: C_p(T) = 68.66 - 0.0212T + 1.295 \times 10^{-6}T^2 - 9687T^{-1} \text{ (J mol}^{-1} \text{ K}^{-1}) \quad (7b)$$

$$\text{VC}_{0.87}: C_p(T) = 65.31 - 0.0118T + 7.562 \times 10^{-6}T^2 - 9041T^{-1} \text{ (J mol}^{-1} \text{ K}^{-1}). \quad (7c)$$

Note that the heat capacity values obtained in the present paper for the vanadium carbide VC<sub>0.87</sub> are very close to the reference data for VC<sub>0.88</sub> [48].

Table 4 furnishes heat capacity values and calculated enthalpy and entropy values for VC<sub>0.79</sub>, VC<sub>0.83</sub> and VC<sub>0.87</sub> carbides over the temperature range from 300 to 1500 K.

Thus, calorimetric measurements in conjunction with results of structural investigations show the formation of ordered V<sub>6</sub>C<sub>5</sub> and V<sub>8</sub>C<sub>7</sub> phases in a non-stoichiometric vanadium carbide to be a first-order phase transition. This agrees with the experimental results [38, 46] and with the theoretical conclusion [4, 26, 29] as to the nature of the MC<sub>y</sub>-M<sub>6</sub>C<sub>5</sub> and MC<sub>y</sub>-M<sub>8</sub>C<sub>7</sub> phase transitions in strongly non-stoichiometric carbides of groups IV and V transition metals.

#### 4. Phase diagram for the V-C system

Although the ordering of a non-stoichiometric vanadium carbide VC<sub>y</sub> has long been studied, the literature does not yet provide a reliable phase diagram that takes into account the formation of ordered phases in the V-C system. The first attempt to plot the portion of the V-C system's phase diagram where ordered V<sub>6</sub>C<sub>5</sub> and V<sub>8</sub>C<sub>7</sub> phases coexist dates back to the authors of [11]. Later Athanasiadis *et al* [38] tried to allow for the phase equilibria in VC<sub>y</sub> over a narrow range of compositions,  $0.84 \leq y \leq 0.93$ , and temperatures  $1273 \text{ K} < T < 1473 \text{ K}$ . In the phase diagrams for the V-C system that are given in [49–51], the region of ordering is shown tentatively and is actually a repetition of the data of [11]. In a recent review article [2] dealing solely with phase diagrams of the M-C and M-N systems with carbides MC<sub>y</sub> and nitrides MN<sub>y</sub> that undergo ordering, the phase diagram of the V-C system is absent altogether since the data available are too scanty to construct one.

A major difficulty in constructing a phase diagram of the V-C system resides in that the upper boundary of the homogeneity region of disordered cubic vanadium carbide VC<sub>y</sub> is the VC<sub>0.88</sub> carbide rather than an MC<sub>1.0</sub> carbide of stoichiometric composition, as is the case with carbides of other transition metals. The unusual position of the upper boundary of the homogeneity region for the VC<sub>y</sub> carbide caused the formation in VC<sub>y</sub> of an ordered M<sub>8</sub>C<sub>7</sub>-type phase that does not exist in other carbides.

The experimental data obtained in the present paper for the temperatures and, most importantly, heats of the V<sub>6</sub>C<sub>5</sub> ↔ VC<sub>y</sub> and V<sub>8</sub>C<sub>7</sub> ↔ VC<sub>y</sub> phase transformations enable allowance for the ordering of the VC<sub>y</sub> carbide in the phase diagram of the V-C system.

Phase equilibria in the region of ordering of a non-stoichiometric cubic VC<sub>y</sub> carbide were calculated by the order parameter functional (OPF) method [1, 4, 26, 43, 52].

Briefly the OPF method consists of the following. The physical basis of this method is the mean-field approximation; as regards its formalism, it is a cluster method, but differs in allowing a detailed treatment of a symmetry of a crystal with any degree of long-range order.

The main feature of the OPF method is the representation of the probabilities of various figures in terms of values of the distribution function  $n_\nu(\mathbf{r})$ , which depends directly on long-range order parameters  $\eta$ . The distribution function  $n_\nu(\mathbf{r})$  is the probability of detecting an atom of species  $\nu$  at a site  $\mathbf{r}$  in the ordering lattice.





It is shown in the OPF method [1, 2, 43] that the free energy of a non-stoichiometric carbide MC<sub>y</sub> with any degree of long-range order is represented as

$$F(y, \eta, T) = F_0(T) + yF_1(T) + P_0^{(2)}F_2(T) - TS_c(y, \eta) \quad (8)$$

where

$$P_0^{(2)} = y^2 - a^{(s)}\eta^2/4t^2 \quad (9)$$

is the probability of finding of a complete pair C–C in the non-metallic sublattice of MC<sub>y</sub> compound discussed;  $F_0$ ,  $F_1$  and  $F_2$  are the energy parameters;  $a^{(s)}$  is the coefficient which depends on the type of superstructure. The configurational entropy of an ordered phase M<sub>2t</sub>C<sub>2t-1</sub> (with  $t = 1, 1.5, 3$  or  $4$ ) is equal to

$$S_c(y, \eta) = -(k_B/2t)\{n_1^{(d)} \ln n_1^{(d)} + (1 - n_1^{(d)}) \ln(1 - n_1^{(d)}) \\ + (2t - 1)[n_2^{(d)} \ln n_2^{(d)} + (1 - n_2^{(d)}) \ln(1 - n_2^{(d)})]\} \quad (10)$$

where  $n_1^{(d)} = y - (2t - 1)\eta/2t$  and  $n_2^{(d)} = y + \eta/2t$  are the probabilities of finding a carbon atom on a vacancy sublattice site and on a site of the carbon atom sublattice, respectively.

It is easy to see that for  $\eta = 0$  the expression (8) with allowance for (9) has the form

$$F(y, 0, T) = F_0(T) + yF_1(T) + y^2F_2(T) - TS_c(y, 0) \quad (11)$$

and describes the free energy of a disordered carbide MC<sub>y</sub>.

A system of equations which describes the equilibrium of a disordered MC<sub>y</sub> and an ordered M<sub>2t</sub>C<sub>2t-1</sub> phase, has the form

$$y_1(2 - y_1) + \frac{k_B T}{F_2(T)} \ln y_1 = y_2(2 - y_2) + \frac{a^{(s)}}{4t^2} \eta_{\text{equil}}^2 \\ + \frac{1}{2t} \frac{k_B T}{F_2(T)} [\ln n_1^{(d)} + (2t - 1) \ln n_2^{(d)}]_{\eta=\eta_{\text{equil}}} \quad (12) \\ y_1^2 - \frac{k_B T}{F_2(T)} \ln(1 - y_1) = y_2^2 - \frac{a^{(s)}}{4t^2} \eta_{\text{equil}}^2 \\ - \frac{1}{2t} \frac{k_B T}{F_2(T)} [\ln(1 - n_1^{(d)}) + (2t - 1) \ln(1 - n_2^{(d)})]_{\eta=\eta_{\text{equil}}}$$

where  $\eta_{\text{equil}}$  is the equilibrium value of the long-range order parameter at a temperature considered. The expression for the equilibrium long-range order parameter  $\eta_{\text{equil}}$  has the form

$$\frac{1}{\eta_{\text{equil}}} \ln \left[ \frac{n_2^{(d)}(1 - n_1^{(d)})}{n_1^{(d)}(1 - n_2^{(d)})} \right]_{\eta=\eta_{\text{equil}}} = \frac{2a^{(s)}}{(2t - 1)} \frac{F_2(T)}{k_B T}. \quad (13)$$

By solving equations (12) for all the binary equilibria which are possible in the ordering carbide we can find the position of the phase boundaries and construct the region of ordering as a part of equilibrium phase diagram.

Detailed description of the OPF method is given in [2].

The free energy  $F(y, 0, T) = F_0(T) + yF_1(T) + y^2F_2(T) - TS_c(y, 0)$  of a disordered cubic VC<sub>y</sub> carbide and the free energy  $F(T)$  of a hexagonal V<sub>2</sub>C<sub>y</sub> ( $\beta$ -V<sub>2</sub>C) carbide, needed for calculation, were found by invoking thermodynamic reference data as well as the results of [20], [23]–[25] and [48]. In the calculation, the ordered V<sub>8</sub>C<sub>7</sub> phase was assumed to possess no homogeneity region. Indeed, according to [22], [38] and our findings, the V<sub>8</sub>C<sub>7</sub> phase alone forms only with the carbide composition VC<sub>0.87–0.875</sub>, whereas at lower carbon concentrations ( $0.83 < y < 0.885$ ) the specimens always contain, along with the V<sub>8</sub>C<sub>7</sub> phase, also the V<sub>6</sub>C<sub>5</sub>

phase, which has a wide homogeneity region. In addition, according to [20] and [46], the  $V_8C_7 \leftrightarrow VC_y$  transition temperature is, within measurement errors, virtually independent of  $VC_y$  carbide composition (see figure 5). The free energy of the  $V_8C_7$  ( $VC_{0.875}$ ) phase was represented as

$$F_{V_8C_7(VC_{0.875})}(T) = F(T) - TS_c + (\Delta H_{\text{trans}}/T_{\text{trans}})(T - T_{\text{trans}}) \quad (14)$$

with  $F(T) = F_0(T) + xF_1(T) + x^2F_2(T)$  at  $x = 0.875$  (the parameters  $F_0(T)$ ,  $F_1(T)$  and  $F_2(T)$  are the same as those for a disordered  $VC_y$  carbide);  $S_c$  the configuration entropy of the  $VC_{0.875}$  carbide;  $\Delta H_{\text{trans}} = 3 \text{ kJ mol}^{-1}$  and  $T_{\text{trans}} = 1380 \text{ K}$  the  $V_8C_7 \rightarrow VC_{0.875}$  transition heat and temperature evaluated on the basis of experimental data. The energy parameters  $F(T)$  of free energies were represented by polynomials of the form

$$F(T) = f_0 + f_1T + f_2T^2 + f_3T^{-1} + f_4T \ln T. \quad (15)$$

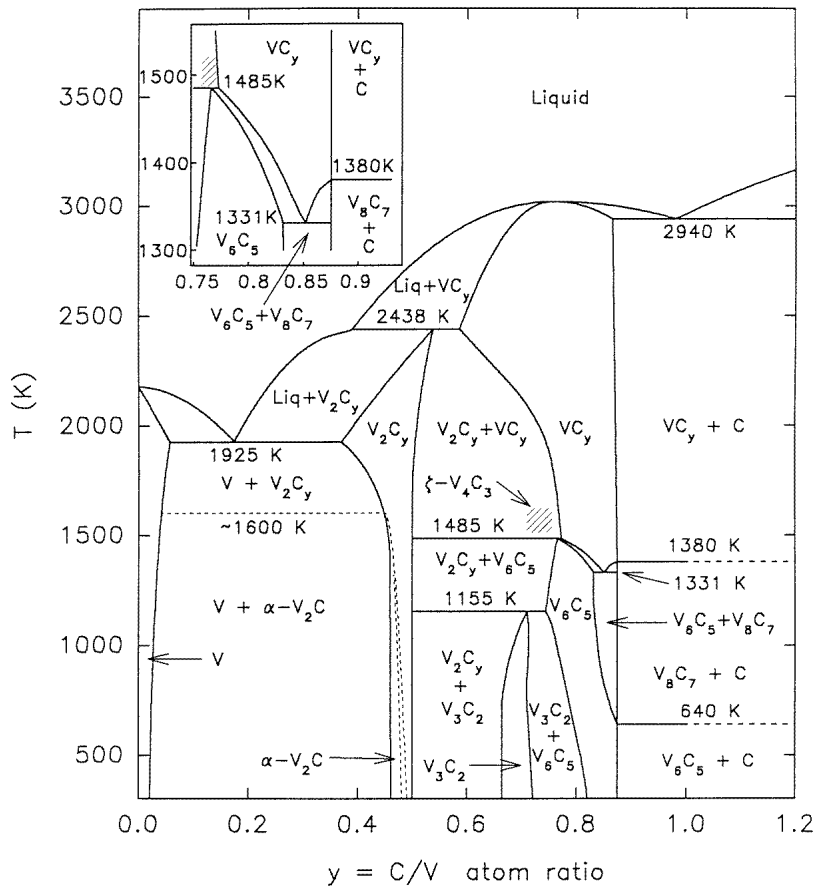
Numerical values of the coefficients  $f_i$  are summarized in table 5.

**Table 5.** Coefficients of the polynomial (9), describing the parameters  $F_0(T)$ ,  $F_1(T)$  and  $F_2(T)$  of the free energy  $F(y, 0, T)$  of the disordered cubic vanadium carbide  $VC_y$  and free energies  $F(T)$  of the lower disordered hexagonal carbide  $V_2C_y$  ( $\beta$ - $V_2C$ ) and ordered carbide  $V_8C_7$  ( $VC_{0.875}$ ).

Phase	Parameter	Coefficients				
		$f_0$ (kJ mol <sup>-1</sup> )	$f_1 \times 10^3$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$f_2 \times 10^6$ (kJ mol <sup>-1</sup> K <sup>-2</sup> )	$f_3$ (kJ K mol <sup>-1</sup> )	$f_4 \times 10^3$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
$VC_y$	$F_0(298\text{--}2000 \text{ K})$	97.09	145.0	-11.84	-208	-26.95
	$F_1(298\text{--}2000 \text{ K})$	-437.49	-86.23	11.75	932	18.29
	$F_2(298\text{--}2000 \text{ K})$	211.36	267.21	0	0	-42.47
$V_2C_y$ ( $\beta$ - $V_2C$ )	$F(298\text{--}1600 \text{ K})$	-180.96	513.67	-1.70	1290	-83.12
$V_8C_7$	$F(298\text{--}1400 \text{ K})$	-123.89	274.13	-1.56	608	-43.46

The phase diagram thus constructed for the V-C system is portrayed in figure 6. From the calculation performed, it follows that the ordering of a non-stoichiometric cubic  $VC_y$  carbide in different temperature and concentration ranges may result in the formation of three ordered phases, viz.  $V_3C_2$ ,  $V_6C_5$  and  $V_8C_7$ .

The principal ordered vanadium carbide phase is the  $V_6C_5$  phase, which is produced at a temperature below 1485 K and has at 1100 K a region of homogeneity ranging between  $VC_{0.745}$  and  $VC_{0.831}$ . This phase may be observed also in two-phase regions, whereby the region of its existence overlaps almost the entire region of homogeneity of the  $VC_y$  carbide (figure 6). An ordered  $V_8C_7$  phase forms at a lower temperature, 1380 K, and may at 1330 K be observed together with  $V_6C_5$  in the two-phase region from  $VC_{0.83}$  to  $VC_{0.875}$ ; this gives a good fit to experimental data [38, 46]. As the temperature is lowered the two-phase region  $V_6C_5 + V_8C_7$ , where the ordered  $V_8C_7$  phase exists, diminishes in width. The ordered  $V_6C_5$  and  $V_8C_7$  phases form a eutectic with  $T_e = 1331 \text{ K}$  and  $y_e = 0.852$ ; these values are very close to estimates [38] according to which  $T_e \approx 1300 \text{ K}$  and  $y_e \approx 0.852$ . Also, the calculation shows that under equilibrium conditions, an ordered  $V_3C_2$  phase with a sufficiently narrow region of homogeneity (from  $VC_{0.68}$  to  $VC_{0.71}$  at 1000 K and from  $VC_{0.665}$  to  $VC_{0.721}$  at 300 K) can arise by the peritectoid reaction  $V_2C_y + V_6C_5 \rightarrow V_3C_2$  in the vanadium carbide at a temperature of 1155 K and under. Up to now this phase has not been observed experimentally. Note that the ordered  $V_3C_2$  phase should not be confused with the rhombic  $\zeta$ - $V_4C_{3-x}$  phase that exists in a concentration interval close to a region of existence of



**Figure 6.** Equilibrium phase diagram of the V-C system with consideration of the ordering of non-stoichiometric cubic and hexagonal vanadium carbides  $VC_y$  and  $V_2C_y$ :  $V_8C_7$ ,  $V_6C_5$  and  $V_3C_2$  are the ordered phases of cubic carbide  $VC_y$ ;  $\alpha-V_2C$  is an ordered phase of lower hexagonal carbide  $V_2C_y$  ( $\beta-V_2C$ ). The inset is the extended part of the ordering region near the upper boundary of the homogeneity region of  $VC_y$ . The position of the phase boundaries outside the region of ordering is shown according to [49] and [50].

the  $V_3C_2$  phase. Calculated values of  $T_{trans}$ ,  $\Delta S_{trans}$ , and  $\Delta H_{trans}$  for phase transformations associated with the ordering of a non-stoichiometric cubic vanadium carbide  $VC_y$  are quoted in table 6.

An ordered rhombic  $\alpha-V_2C$  phase forms in the region of homogeneity of the lowest hexagonal vanadium carbide  $V_2C_y$  ( $\beta-V_2C$ ) [17, 18]. The exact ordering temperature is not known; according to [49, 50] it is under 1870 K. When measuring the magnetic susceptibility of an ordered  $\alpha-V_2C$  carbide in the range 300–1300 K, the  $\alpha-V_2C \rightarrow V_2C_y$  ( $\beta-V_2C$ ) structural phase transition could not be pinpointed even at temperatures as high as 1300 K [53]. On the strength of the data [49, 50, 53], the  $\alpha-V_2C \rightarrow V_2C_y$  ( $\beta-V_2C$ ) order–disorder phase transition temperature given in the phase diagram for the V-C system (figure 6) has a tentative value of ~1600 K. In 1992 a new compound,  $V_8C_{12}$ , was detected in the V-C system, which is a molecular cluster [54]. In the phase diagram constructed for the V-C system, this compound is not shown as it lies outside the composition range involved.

**Table 6.** Thermodynamic characteristics of order–order and order–disorder phase transitions for vanadium carbide  $VC_y$ .

y	$V_3C_2 \rightarrow V_6C_5$			$V_6C_5 \rightarrow VC_y$			$V_8C_7 \rightarrow VC_y$		
	$T_{trans}$ (K)	$\Delta S_{trans}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_{trans}$ (kJ mol <sup>-1</sup> )	$T_{trans}$ (K)	$\Delta S_{trans}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_{trans}$ (kJ mol <sup>-1</sup> )	$T_{trans}$ (K)	$\Delta S_{trans}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_{trans}$ (kJ mol <sup>-1</sup> )
0.73	1138	1.38	1.57	—	—	—	—	—	—
0.74	993	1.17	1.16	—	—	—	—	—	—
0.75	728	0.82	0.60	—	—	—	—	—	—
0.752	625	0.73	0.46	—	—	—	—	—	—
0.755	<300	—	—	—	—	—	—	—	—
0.77	—	—	—	1481	1.75	2.59	—	—	—
0.78	—	—	—	1467	1.85	2.72	—	—	—
0.79	—	—	—	1450	1.96	2.84	—	—	—
0.80	—	—	—	1432	2.05	2.93	—	—	—
0.81	—	—	—	1412	2.13	3.01	—	—	—
0.82	—	—	—	1390	2.18	3.04	—	—	—
0.83	—	—	—	1366	2.21	3.02	—	—	—
0.833	—	—	—	1357	2.21	2.99	—	—	—
0.84	—	—	—	1338	2.20	2.95	—	—	—
0.875	—	—	—	—	—	—	1380	2.17	3.00

Thus all disorder–order phase transitions in the vanadium carbide  $VC_y$  are the first-order phase transitions. A similar conclusion has been drawn by the authors of investigation [55]. For the  $VC_{0.79}$  carbide, the calculated temperature  $T_{trans}$  and heat  $\Delta H_{trans}$  of the  $V_6C_5 \rightarrow VC_{0.79}$  transition are equal to 1450 K and 2.84 kJ mol<sup>-1</sup>, the experimental value of  $\Delta H_{trans}$  (table 3) is slightly lower because, judging from calorimetric measurements, a small amount of  $\zeta$ - $V_4C_{3-x}$  phase forms in the  $VC_{0.79}$  carbide.

## 5. Conclusions

As a whole, the study that we have made of the crystal structure and heat capacity of a non-stoichiometric vanadium carbide  $VC_y$  ( $0.66 \leq y \leq 0.88$ ) shows that the ordering of vanadium carbide leads to the formation of an ordered  $V_6C_5$  and  $V_8C_7$  phases. The  $V_6C_5$  phase possesses a monoclinic (space group  $C2/m$ ) or a trigonal (space group  $P3_1$ ) structure and a homogeneity region from  $VC_{0.75}$  to  $VC_{0.83}$  (at 1100 K). The cubic (space group  $P4_332$ ) ordered  $V_8C_7$  phase has virtually no homogeneity region or its homogeneity region is very small (from  $VC_{0.87}$  to  $VC_{0.875}$  at 1300 K); the  $V_8C_7$  phase can be observed together with  $V_6C_5$  in the two-phase region  $VC_{0.83}$ – $VC_{0.875}$ . In the  $C_p(T)$  curves for the carbides studied, the presence of discontinuity points in the region of reversible equilibrium disorder–order transitions provides direct evidence that the  $V_6C_5 \leftrightarrow VC_y$  and  $V_8C_7 \leftrightarrow VC_{0.875}$  phase transformations are first-order phase transitions. According to experimental data, the temperatures for the above transitions are 1400–1450 and 1360–1380 K, respectively.

Our thermodynamic model for ordered  $VC_y$  carbide predicts that the  $V_6C_5 \leftrightarrow VC_y$  transformation temperature varies from 1480 to 1340 K as the composition of the  $VC_y$  carbide is varied from  $VC_{0.77}$  to  $VC_{0.84}$ . A calculation of the equilibrium phase diagram of the V–C system has shown that as a cubic  $VC_y$  carbide undergoes ordering ordered  $V_3C_2$ ,  $V_6C_5$  and  $V_8C_7$  phases may form in the various different temperature and concentration intervals. The  $V_3C_2$  phase displays a very narrow homogeneity region and forms as a result of a peritectoid

transformation at a temperature below 1155 K. The main ordered phase of the VC<sub>y</sub> carbide is the V<sub>6</sub>C<sub>5</sub> phase, which has a sufficiently wide region of homogeneity. The cubic V<sub>8</sub>C<sub>7</sub> superstructure possesses virtually no homogeneity region and can occur together with the V<sub>6</sub>C<sub>5</sub> phase in the two-phase region at 1330 K > T > 640 K.

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