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Polytype formation in nonmetallic substances

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Abstract. A systematic account is given of the known data on polytypism in nonmetallic substances with various structures. The existing hypotheses concerning the nature of polytypism are discussed. It is shown that polytype formation in nonmetallic crystals is a solid-state relaxation rearrangement accompanied by the formation of planar defects of various types, inducing the breakdown in the periodicity of the packing of atomic layers. Such defects and hence structural elements of polytypes may be structural (growths, deformation) and chemical packing defects, microtwins, antiphase boundaries, layers of vacancies, as well as layers of other phases coupled coherently with the basic structure. For diamond-like phases (SiC, AlN, BN), intragranular polytype transformations, induced by the migration of boundaries, occur together with intragranular polytype transformations. The bibliography includes 294 references.

I. Introduction

As a property of crystalline solids, polytypism is determined by the possibility that a given substance may exist as a multiplicity of structural forms differing in the packing of identical layers, which are structural elements of the basic lattice. Whereas the characteristic of the latter is the interlayer distance (c_0), the characteristic of the polytype lattice is the distance between blocks (C), which consist, of several layers (n) of the basic lattice:

$$C = nc_0 .$$

When n is an integer, one is dealing with commensurate polytypes, while in the case of fractional n the polytypes are noncommensurate.

In terms of the type of ordering, polytypes can be divided into two kinds: ordered polytypes with a distinct repeatability of the blocks and non ordered polytypes [one-dimensionally disordered state (ODS)] distinguished by the fact that the blocks with different C are arranged in a random fashion, *i.e.* without periodicity.

A multiplicity of ways of designating polytypes, reflecting their structure, are known.[1–3] The Ramsdell designations are most often employed as the simplest and clearest. The designation includes the number of layers in the unit cell and a letter indicating the type of symmetry of the cell: H — hexagonal, R — rhombohedral, T — trigonal. For example, 6H is a polytype with a six-layer repeat period along the c axis and a primitive hexagonal cell. For rhombohedral polytypes, the number of layers is a multiple of three.

A new method of describing polytypes as structures with different numbers and types of regular systems of points has been proposed recently.[4] Bokii and Laptev[4,5] examined in detail the approach to this kind of description in relation to ZnS, CdI_2, TiO_2, and certain silicates. However, this method of describing polytypes has not as yet found extensive application.

For the majority of polytypes, the repeat period of the layers varies in one direction. For this reason, polytypism is frequently referred to as one-dimensional polymorphism.

Verma and Krishna[2] defined polytypism as the ability of a substance to crystallise in several different modifications and in all these modifications two unit cell parameters are identical, whilst the third is a variable integral multiple of the same quantity. The structural state of polytypes should also correspond to three essential conditions: firstly, polytypic forms must consist of identical structural units and differ only in the packing of the layers; secondly, each layer should have one chemical composition corresponding to the stoichiometric composition of the crystal; thirdly, each pair of neighbouring layers is equivalent. The foregoing refers to the classical definition based on the study of polytypism in ten single-crystal substances. The compounds examined include SiC, ZnS, CdI_2, PbI_2, $CdBr_2$, AgI, *etc.*, which had been regarded previously as strictly stoichiometric. The above definition of polytypism was formulated when noncommensurate polytypes had not yet been observed.

Extensive experimental data confirming the tendency towards polytype formation in crystalline solids differing in the types of chemical bonding, crystal lattice, the number of different atoms (substances ranging from monatomic, for example diamond and carbon, to pentaatomic and hexaatomic in minerals) have now accumulated. Accordingly, it has been established that polytypism is characteristic of various classes of substances: metals, ceramics, minerals, intermetallic compounds, and organic substances. It has been observed in the study of not only single crystals but also films, powder particles, and polycrystalline conpact materials. Polytype formation is very often associated with the nonstoichiometry of substances. Nonstoichiometry in substances such as SiC,[6] ZnS,[7] CdS,[8] *etc.* has also been discovered.

Thompson[9] defined polytypism as a special kind of polymorphism in which new modifications arise as a result of different types of packing of structurally compatible units. In other words,

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polytypes are variants of the packing of simple elements characteristic of the basic structure. In contrast to the definition of polytypism given by Verma and Krishna,[2] in this definition the condition of the structural and chemical identity of the structural elements in the polytype is not obligatory.

In 1984, the Commission of the International Union of Crystallographers proposed a new definition: polytypism is 'the phenomenon of the existence of elements or compounds in the form of two or more multilayer crystalline structures differing in the sequence in which the layers are packed. The layers need not necessarily be crystallographically identical but they should be similar. Polytypism differs from polymorphism by allowing small differences between the chemical compositions of structures not exceeding 0.25 atom per formula unit of any constituent element. Layered structures which differ from one another to an extent greater than this are referred to as polytypoids rather than polytypes'.[10] However, this terminology has not, found extensive application nowadays. As a typical example, one may quote aluminium nitride, for which a relation between composition and multilayer structures has been established. On the other hand, the latter are referred to as polytypes and rarely as polytypoids or pseudopolytypes.

Polytypism was first observed in 1912 by Baumhauer[11] in SiC single crystals. However, the study of this phenomenon did not begin until 1940. At the beginning of the 1950s, the first theory of polytypism appeared (Frank's theory). It referred to the formation of polytypes in the growth of crystals and was therefore called the growth theory. It was based on the hypothesis of the decisive role of screw dislocations in the formation of polytypes with different numbers of layers, in particular the hypothesis that the period of the polytype is determined by the height of the growth step. This theory described satisfactorily the appearance of short-period polytypes in the growth of crystals but could not account for the appearance of long-period structures. The first review of polytype formation in crystals, in which the above theory was also considered, was written by Verma and Krishna.[2]

Extensive data have now accumulated on the phenomenon of polytypism in crystalline solids of different classes and on the possible mechanisms of its occurrence. The physical and chemical nature of this phenomenon has aroused much interest as a fundamental property of crystalline solids. The practical aspect of this phenomenon is also important. The theoretical and experimental data available at present on polytypism indicate that this phenomenon may be determined by a multiplicity of factors. It is also evident that there cannot be a single mechanism of polytype formation. This is indicated also by the fact that the change in the lattice periodicity in crystals may be induced (as will be shown below) by the formation of planar defects of different nature — structural and chemical packing defects, growth and deformation microtwins, antiphase boundaries, layers of outcrops of other phases, layer-by-layer changes in the coordination numbers and packing motifs of the constituent atoms, *etc*.

The majority of data on polytypism in metallic materials, including pure metals (only the lanthanides), alloys, intermetallic compounds, including Laves phases (compounds of the type AB_2), and ordered alloys, have been surveyed in monographs[3,12]. In these communications, Nikolin[3] identified two kinds of polytypes: stable, formed on crystallisation or annealing at a high temperature, and unstable formed as a result of martensite transformations. For certain Laves phases and ordered alloys (for example in the Cu–Au, Ag–Mn, and Pd–Mn systems), a relation was discovered between the modulation period of long-period structures and the average number of valence electrons per atom, the so called electron concentration e/a (e is the total number of valence electrons and a the number of atoms in the unit cell). On the basis of these data, it was concluded[3] that polytype formation in metallic crystals is determined by the band factor, *i.e*. by their band structure.

In recent years, the diversity of polytypic structures and their stability in crystalline solids have been considered on the basis of the model description taking into account the competitive nature of the interaction between structural units (blocks or polyhedra), the different variants of the packing of which actually determine polytype formation, including two- and three-dimensional polytype formation. The Frenkel'–Kontorova and Ising (spin model) models are best known.[13,14] The latter is based on the idea of the decisive role in polytype formation of the exchange interaction between the first and subsequent structural units as the basic elements of the crystal lattices of solids (the ANNNI model — Axial Next Nearest Neighbour Ising).

The principal postulates on which the model is based are as follows: polytypes are regarded as a series of different variants of the packing of structurally compatible modules (structural units); the structural units are formed on the basis of coordination polyhedra; the polytype formation and the stability of polytypes are a consequence of the change in the effective energy of the interaction between the structural units; the effective energy is a function of pressure, temperature, and chemical composition of the medium. The agreement, between the model considered and a real system has been demonstrated in relation to the polytypic structures of spinelloids. A satisfactory agreement is observed also for compounds such as SiC and ZnS.[13–15] The possibility of applying this model to account, for the polytypism in solid solutions of metals with a hexagonal close-packed lattice has been demonstrated.[16,17]

II. Polytypism in nonmetallic crystals

The available information about the polytypism in nonmetallic crystals having the compositions MX and MX_2 (SiC, ZnS, CdI_2, *etc*.), published up to 1966, has been surveyed.[2] Certain data on polytypes in minerals can be found in two communications.[2,18] Extensive information about the polytypism in such materials has now accumulated.

Polytypism as a physical phenomenon in nonmetallic substances may be classified in terms of various features: the thermodynamic conditions under which it occurs, the type of planar defects inducing an ordered alternation of blocks of layers, the classes of substances with an identical type of chemical bonding or crystal lattice, and also the properties and applications of the substances. The classification taking into account the features specified constitutes an independent task. Bearing in mind the discovery of polytypism as a growth phenomenon and its subsequent observation in crystals obtained under various conditions, one may identify four groups of polytypism: growth, thermal, deformation, and concentration. The above terminology reflects the nature of the principal factor governing polytype formation, although in the majority of cases its development is determined by a combination of many factors. Furthermore, such subdivision is suitable only for the group of substances with diamond and diamond-like phase (wurtzite and sphalerite) lattices. The above kinds of polytypism occur in precisely these substances. For example, growth polytypism is characteristic of SiC, ZnS, C (graphite), C (lonsdaleite), Si, and CdS; thermal polytypism is characteristic of SiC, ZnS, and 2H BN, concentration polytypism is characteristic of SiC, ZnS, AlN, ZnO, BeO, and $BeSiN_2$, and deformation polytypism is characteristic of SiC, ZnS, CdS, C (diamond), 2H BN, 3C BN, and Si (the polytypes are formed on the basis of 3C and 2H phases for SiC, ZnS, and CdS, the 3C phase for Si, and the 2H phase for AlN, BeO, ZnO, and $BeSiN_2$). For other substances, the combination of such varieties of polytypism is not observed.

Since we shall subsequently discuss briefly also the practical aspect of polytypism in non metallic materials, it is useful to analyse the problem of polytypism as a whole for different groups of materials differentiated in inorganic chemistry as carbides, nitrides, oxides, *etc*. Henceforth we shall consider polytypism in individual groups of substances, but we shall note beforehand certain data on polytypism in organic substances and shall also describe the available information about this phenomenon in

monatomic substances; the polytypism in transition metal carbides and nitrides of the type of interstitial phases[19] will be considered jointly.

The possibility of the formation of polytypes in organic substances was first pointed out by Verma and Krishna.[2] The direct observation of polytypes by high resolution microscopy in crystalline organic substances (in relation to phthalocyanine) has been reported by Howitt.[20] The formation of phthalocyanine polytypes was accompanied by the $\beta \rightarrow \alpha$ shear transformation. Zorkii and Nesterova[21] observed intralayer polytypism in the selenium-containing organic substances $C_{16}H_{16}O_4Se$ and $C_{13}H_{10}N_4Se$. Its characteristic feature is that blocks having identical outer layers and differing in the structure of the 'core' arise in the structure of the initial substance. As a result, there is a possibility of the formation of homolayer (made up of identical layers) and heterolayer (made up of different layers) structural fragments.

1. Monatomic substances

Silicon and carbon belong to the class of monatomic substances tending to exhibit polytypism. Polytype formation in germanium has been mentioned[22] but we are not aware of any concrete information.

a. Silicon

Silicon polytypes have been observed in an electron microscope study of its formations in the form of whiskers and fibres obtained by the decomposition of SiH_4 at 500–520 °C on gold-covered silicon supports.[23] The experimental and calculated unit cell parameters are virtually the same for the identified polytypes.

Polytype	6H	27R	51R	141R
c(calculation) /Å	18.84	84.65	159.89	442.05
c(experiment) /Å	18.59	84.61	160.07	442.29

The formation of polytypes on deformation of silicon is apparently also possible. This is indicated by data on the intense disordering of the Si structure with the diamond lattice on impact application of a load and the formation on subsequent annealing of the 2H modification from this structural state.[24] Data on the 3C → 2H transition in silicon at a high pressure[25] and following the application of a concentrated load, *i.e.* under the indentor,[26] are available. The above transition occurs also when a large number of arsenic ions are implanted in a silicon support.[27]

b. Carbon

Three polymorphic modifications — graphite, lonsdaleite (hexagonal diamond), and diamond — are characteristic of crystalline carbon. They all tend to form polytypes.

The commonest polytype for graphite is 3R; the formation of polytypes 6R, 10H, and 12H is also possible.[28,29]

The formation of a mixture of multilayer polytypes (MP) in lonsdaleite deformed at high pressures and temperatures (T = 1800 °C, P = 7.7 GPa) under conditions involving the formation of a polycrystalline diamond material has been observed in microdiffraction studies.[30] The presence of MP was indicated by a system of point reflections on continuous $h0l$ rows on the electron microdiffraction pattern of sections of the type $(11\bar{2}0)$ through lonsdaleite particles. Subsequently the 6H polytype of lonsdaleite, formed on deposition of carbon films from the gas phase, was identified by electron microscopy.[31] Calculated X-ray diffraction data for a series of lonsdaleite polytypes (3C, 2H, 6H, 4H, 8H, 10H, 15R, and 21R) have been published.[32]

The possibility of the formation of MP from cubic diamond is indicated by the studies of Britun *et al.*[33] The presence of a set of nonsystematic point reflections (in rows parallel to 111) on the electron diffraction pattern of the {110} sections of diamond grains deformed at $T > 2200$ °C and P = 8–10 GPa has been established. The density of the disperse twins on one plane of the type {111} on the diffraction pattern, extending from boundary to boundary, is usually high in grains of this kind. These twins are formed as a rule only on deformation.

In the crystallisation of carbon from the gas phase, the regraphitisation of diamond, and laser irradiation of graphite, a variety of the carbon phase is formed — carbynes. Carbynes are regarded as linear carbon polytypes.[34] Such structures have been classified on the basis of various parameters: the linear relation between the number of atoms in the chain and the length of the c axis, the unit cell volume, and the ratio a/c.

2. Silicon carbide

It was noted above that SiC was the first substance in the study of which polytypism was observed as a physical phenomenon.[11] So far more than 150 polytypes with hexagonal, rhombohedral, and tetragonal symmetries have been identified in SiC. The parameter c in these polytypes varies from 0.5 nm for 2H to 1200 nm for 4680R. The polytypes observed up to 1966 have been described by Verma and Krishna[2] and data on polytypes found later are contained in papers published in periodicals.

The SiC polytypes are distinghished by the ratio of the carbon and silicon concentrations and hence by the X-ray density and the concentration of vacancies (Table 1). The silicon concentration should be 70.05 mass% for stoichiometric SiC, while for 3C SiC it is 71.04 mass% and for 6H SiC it amounts to 70.7 mass%. The data obtained in studies of the nonstichiometry in SiC have been surveyed.[35]

The polytypic transformations in SiC may occur under different thermodynamic conditions: only on heating (both in an inert medium and in the presence of impurities dissolving in the lattice), on application of different types of load (rubbing at room temperature, treatment by application of heat and pressure, bending, and a concentrated load under the indentor), and under the conditions of the implantation of impurities and subsequent annealing. Thus all known types of polytypism, occurring in the group of diamonds-like phases, are characteristic of SiC.

Table 1. Characteristics of certain silicon carbide polytypes.

Polytype	D	q	[Si]/[C]	$10^{-20}N$ /cm^{-3}		h /eV
				N_{Si}	N_C	
3C	0	0.74	1.046	2.0	2.3	2.2
8H	0.25	0.96	1.029	3.3	1.7	2.56
21R	0.29	–	–	–	–	2.77
6H	0.33	1.22	1.022	4.3	1.5	2.86
33R	0.36	–	–	–	–	–
15R	0.40	1.19	1.012	5.7	1.1	2.9
10H	0.40	–	–	–	–	–
27R	0.44	1.30	1.008	6.2	1.0	–
4H	0.5	1.37	1.001	7.1	0.7	3.1

Note. The following designations have been adopted: D = degree of hexagonality, q = effective charge on the silicon atom, N = concentration of vacancies, h = width of the forbidden band. The forbidden band widths have been taken from Knippenberg[36] and the remaining parameters from Tsvetkov[6].

A multiplicity of publications have been devoted to the polytype formation in SiC during growth and also partly during post-heat treatment (see, for example, Refs 2 and 36–40). We shall deal briefly only with questions of the stability of the basic polytypes, including those arising on doping and deformation.

The two-layer (2H) wurtzite SiC phase is known, but its formation during growth and treatment is rarely observed. This form was first noted in the gas-phase deposition of SiC at 1400–1500 °C in hydrogen.[41] Subsequently it was identified in combination with 3C SiC on nitrogenation of powdered silicon

pellets placed on a graphite support [42] and also on decomposition of Si_3N_4 in nitrogen with an admixture of CO.[43] The stabilisation of the 2H SiC phase has been explained by the dissolution of oxygen.[44] Under the conditions of uniaxially oriented [slip along the $\langle 0001\rangle\langle 10\bar{1}0\rangle$ system] application of a load to SiC crystals at 1600 – 1800 °C, transitions from the 6H and 3C phases to the 2H phase are possible.[45]

The formation of the 2H phase is also observed in polycrystalline materials formed from SiC in the presence of oxygen and also aluminium or magnesium.[46,47] This phase is extremely unstable. Its transition to the ODS or the two-phase (2H + 3C) state, characterised by a high concentration of packing defects (PD), occurs already at $T > 400$ °C.[48]

The 3C SiC form is assumed to be stable at $T < 1400$ °C. At higher temperatures (both in the presence of impurities such as B and Al and without them), it is converted into the 6H polytype. The 6H polytype is the high-temperature ($T > 2000$ °C) stable form of SiC in an inert gaseous medium. This has been confirmed convincingly in a study [36] where it was established that the 6H polytype is formed in greatest amount in the synthesis of SiC from SiO_2 and C in the range 2000 – 3000 °C.

Numerous studies (see, for example, Refs 49 – 52) have shown that the aluminium and boron impurities (in the form of elemental phases or the compounds Al_2O_3, B_4C, and BN) promote the 3C → 6H → 4H and 3C → 4H transitions. The conversion into the 4H polytype occurs at $T > 1800$ °C; at $T > 2000$ °C, this polytype becomes dominant. It has been suggested that the aluminium and boron impurities stabilise the 4H polytype. The action of the above impurities is most effective in combination with added carbon. According to Tajima and Kingery,[53] aluminium and boron dissolve in the SiC lattice with formation of substituional solid solutions and boron can substitute both silicon and carbon. The positive role of carbon n the polytypic transitions in SiC has been explained [54] by the operation of two factors: the removal of the oxygen film from the surface of the crystals and the increase in the concentration of vacancies.

The transitions between the 3C and 6H phases, occurring within crystallites under different conditions (only on heating, on heating accompanied by doping, and on deformation), occur in most cases *via* a series of heterophase (3C + 6H + MP) states differing in the number of phases. The individual phases and polytypes are represented by plates limited by close-packed (111) and (0001) planes, which determines the microdomain structure of the heterophase crystals (Fig. 1). Monopolytypic crystals can form only after prolonged annealing: for example, in the 3C → 6H transition which is of the single crystal of the initial phase → single crystal of the final phase type.[55] A similar transition has been observed also in the transformation of 2H SiC in the form of whiskers into a lamellar single crystal of the 3C phase.[37]

Numerous data indicate that nitrogen stabilises the 3C phase. This is manifested by the fact that, during the annealing of 3C SiC even at 2600 °C under nitrogen pressure (66.5×10^3 N m^{-2}), the transformation to multilayer structures does not occur.[56] In the case of the initial 6H phase, the 6H → 3C transformation takes place on annealing under nitrogen pressure [$(0.1-3) \times 10^6$ N m^{-2} (Jepps and Page) [57] and 4×10^6 N m^{-2} (Kieffer and Gugel)] [58] and also on hot pressing in the presence of added nitrides.[59] The formation of the 3C phase is then accompanied by the appearance of twins in the latter.

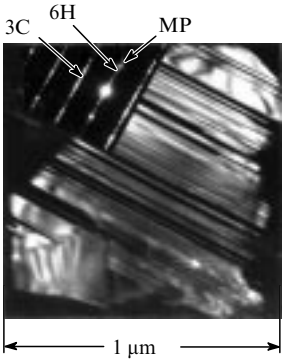


Figure 1. The structure of the heterophase (6H + 3C + MP) SiC crystal.

The 6H → 3C transformation occurs also during annealing above 2000 °C in a silicon-containing medium [55] as well as on deformation. In the latter case, this is possible on rubbing at the normal temperature,[60] on uniaxial loading in the range 1800 – 2000 °C,[45] and at a high pressure (1 – 10 GPa) starting from a temperature of 400 °C.[61–63] Britun *et al.*[64] established for the first time that this transformation is reversible at $P = 7.7$ GPa and $T > 2000$ °C. The direct 6H → 3C and reverse 3C → 6H transformations in the grains are crystallographically similar: the close-packed planes and directions in the initial final phases are parallel — $(0001)||(111)$; $[11\bar{2}0]||[110]$.

The polytypic transitions in SiC take place also as a result of implantation. In most cases, marked disordering (the establishment of the ODS) or amorphisation take place after such a procedure. It is believed [65] that, on insertion of aluminium into epitaxial 6H SiC layers (at 1400 °C), the 6H→3C transformation occurs. It has been suggested that this is achieved *via* a disordered state. The formation of a twinned 3C phase has been observed after the post-annealing of the 4H + 6H crystals with implanted nitrogen.[66] It is believed that, on implantation of copper in the SiC ceramic, a polytypic transformation in the surface layers also takes place.[67] It has been established [68] that the implantation of boron and aluminium ions in the surface layers of 6H SiC crystals from the side of the (0001) plane leads to amorphisation. On subsequent annealing, a mixture of the 6H + 3C phases or only the 3C SiC phase is formed depending on the irradiation dose and temperature.

The study of polytypism began more than 50 years ago with the investigation of silicon carbide. However, hitherto the nature of the polytypism in SiC has not been established. There are numerous theories, hypotheses, and simply views on this question. We shall only indicate the principal ideas underlying the treatment, of the polytypism in SiC.

The first (dislocation) theory of the polytypism in SiC (and of the phenomenon as a whole) has been proposed by Frank. It is based on the idea of the decisive role of screw dislocations in the formation of polytypes during the growth of crystals. Since this theory was first published jointly with Burton,[69] it is associated also with his name. The polymeric theory of Ramsdell and Kohn explains the appearance of polytypes by the growth of crystals on various atomic (polymer) groups. According to Jagodzinski's thermodynamic theory, the nature of polytypism is accounted for by the vibrational entropy effect. Schneer considered polytypic transformations as second-order transitions on the basis of the available data concerning the energy differences between polytypes. According to Peibst, polytype formation is associated with the thermal vibrations in the structure of the growing crystal. Knippenberg drew attention to the differences between the widths of the forbidden band in the SiC polytypes and therefore concluded that the electron energy plays a decisive role in polytype formation. The above theories have been examined in detail by Verma and Krishna.[2]

In the subsequent attempts to account for the polytypism in SiC, a decisive role was attributed to the structural packing defects generated in the transformations in the solid state during periodic slip or creep dislocations [70] and also those arising at the site of contact between the layers of polytypes growing at the boundary of the twinned crystals of the 3C phase.[71] Direct confirmation of the decisive role of packing defects and twinned crystals of the 3C phase along the (111) plane in the 3C → 6H transition in crystals has been obtained in an electron microscope study of thin foils.[72]

Data on the energy of the packing defects (EPD) along the (0001) plane are available only for 6H SiC. They are extremely scattered: from 1.9 ± 0.25[73] to 13.00,[74] 45–65,[75] and 72 ± 34 mJ m^{-2} at 20 °C.[76] It has also been established[76] that the EPD of the 6H SiC phase increases with increase in temperature from 0.4 mJ m^{-2} at 1100 °C to 0.45 ± 2 mJ m^{-2} at 2000 °C. No information is available about the influence of impurities and deformations on the EPD. However, our studies indicate that the polytypic transformations on doping 6H SiC crystals with boron and aluminium and also on deformation by the application of a high pressure ($P = 4-10$ GPa at 1200–2000 °C) are always preceded by the appearance of a high concentration of basic packing defects. The latter are a diagnostic sign of a decrease in the energy of the packing defects. The relation between the probability of the formation of the packing defects (α) and the EPD (γ) assumes the following form:[77]

$$\alpha = \frac{Gb^2h}{24\pi}\frac{\rho}{\gamma},$$

where G is the modulus of shear, b is the Burgers vector, h is the interplanar spacing, and ρ is the density of dislocations.

It has been suggested that the polytypes in SiC can be formed as a result of martensite transformations.[6] However, experimental conformation of the operation of this mechanism has not been obtained.

It has been suggested that the hexagonal SiC polytypes be regarded[78] as a twinned 3C phase with different concentrations of twinned crystals. Twinned crystal seams in such a phase consist of 2H SiC layers. On this basis, all polytypes (with the exception of 2H) may be regarded as phases differing in the amount of 3C SiC. The 3C SiC content in different polytypes varies from 50% to 75%; the greatest amount of 3C SiC (75%) is present in the 8H polytype. Similar ideas concerning the structure of polytypes with different numbers of layers had been put forward earlier by Ramsdell,[79] who suggested that multilayer polytypes are formed from basic 6H and 15R structures as a result of the breakdown of the packing periodicity in the latter. Data on the structures of long-period SiC polytypes, obtained in electron microscope studies of crystals by the direct lattice resolution method may serve as confirmation of these ideas. According to the results of Dubey and Singh,[80] the 126R polytype consists of blocks of rhombohedral polytypes with a smaller number of layers — 33R, 32R, and 48R, formed on the basis of the 6H, 15R, and 12R cells. It has been established[81] that the 201R polytype is formed from the 6H, 15R, and 8H cells.

As already mentioned, the polytypism in SiC has been treated on the basis of the ANNNI model.[15] Cheng *et al.*[82] later developed a new approach in order to explain the appearance of SiC growth polytypes as equilibrium phases. It is based on the model of the long-range interaction between layers controlled by the background lattice energy. The principal factor is then the postulate that all polytypes may be formed as a result of different types of packing of diatomic SiC layers in the [111] direction of the 3C modification.

Analysis of data on the polytypic transformations in SiC crystals on heating and primarily under doping conditions demonstrates the important role of point defects. Indeed, in most cases (with the exception of heating in N_2) the 3C → 6H transformation takes place. In the initial 3C structure there is an excess of silicon and hence of carbon vacancies (Table 1). Impurities which actively influence the polytypic transformations in SiC dissolve in the SiC lattice also with formation of vacancies. Evidently, on dissolution of B, Al, and N in SiC, heterovalent substitution occurs. The charge compensation in the lattice is then ensured by the formation of vacancies in one of the SiC sublattices[83] and the formation of complexes on the basis of the vacancies is inevitable.† If the vacancies as constituents of the SiC structure participate in polytype formation, the above process may be considered from the standpoint of nonstoichiometry *i.e.* as a transformation in a AlN solid solution. An indirect, confirmation of this hypothesis exists. We have established that the 6H → 4H (in the presence of boron or aluminium) and 2H AlNO → MP (*i.e.* a transformation in a AlN solid solution) transformations in polycrystalline materials are crystallographically and morphologically similar: the final polytypic structure is formed in a layer bounded by basal planes and enriched by the dissolved impurity (Fig. 2).

We may note the characteristic features of the 3C→6H and 3C → 6H → 4H transformations in polycrystalline SiC materials which we established. The transitions occur not only within but also between the grains in the stage involving the recrystallisation enlargement of the grains.

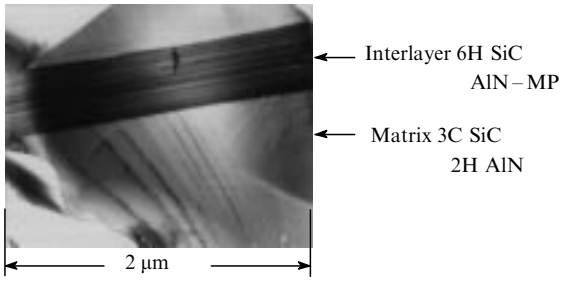


Figure 2. The substructure formed in the SiC and AlN crystals in polytypic transitions (in 6H SiC → 4H SiC under conditions involving doping with boron, in AlN in the course of the transition 2H AlNO → MP).

In the first case, they are crystallographically oriented: under these conditions, the final polytype (it is usually formed in combination with MP in the initial stage of the transition) is segregated in the form of a single plate (0.5–1 μm thick) intersecting the grain from boundary to boundary (Fig. 2). The shape factor for such a plate (the ratio of the length l to the width d) can reach 10–20. The plate is bounded by the basal planes and is coupled *via* these planes to the matrix (initial) phase. The formation of such structural states in the grains induces their anomalous growth and subsequently also the appearance of the grains of the final phase in the form of plates. In the course of the growth of the grains, polytypic transformations of the second type, characterised by the migration of the boundaries between grains made up of different polytypes, occur. Bearing in mind the nature of the mass transfer, determining the migration of the grains, one can postulate that such transformations take place *via* a diffusion mechanism. Fig. 3 presents schemes for the changes in the microstructure of the SiC materials obtained under the conditions of the polytypic transitions indicated. Evidently, depending on the structure of the growing grain, not only forward but also reverse (6H → 3C and 4H → 6H) transitions of the diffusion type may occur in the course of the collective recrystallisation. The evolution of the microstructural development of the SiC material in the case of such transitions is analogous to that observed in the AlN materials obtained in the 2H AlN → MP transitions;[85] for SiC and AlN, these questions have been discussed in detail.[86] Such unusual shape formation in the subgrain structure and among the anisometric (lamellar) grains in SiC (as well as AlN), induced by polytypic transformations, promotes the formation of self-reinforced materials.[87]

3. Aluminosilicon carbide

Two polytypes of aluminosilicon carbide, differing in the content of constituent atoms, are known: 8H Al_4SiC_4 and 15R $Al_2Si_2C_5$.

† The conclusion that such complexes are formed in SiC on dissolution of boron and aluminium has been reached[84] on the basis of data on the rate of diffusion of the above impurities in SiC.

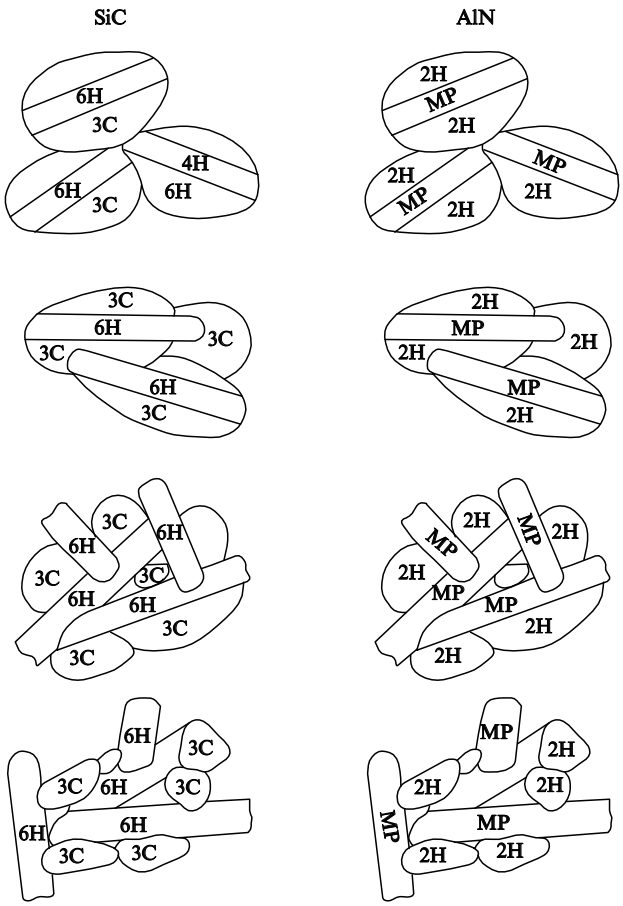


Figure 3. Variation of the granular structure during the development of intergranular polytypic transitions in SiC and AlN.

They have been detected in the products of the interaction of the AlC – SiC mixture[88] and the natural montmorillonite-polyacrylonite mixture.[89] The determinations of the cell size and of the interlayer distance led to the conclusion[90] that the structure of the aluminosilicon carbide may be produced by the substitution of AlN layers by SiC layers in carbonitrides of the type Al_5C_3N and $Al_6C_3N_2$. The latter belong to the class of compounds with the general formula $(AlN)_nAl_4C_3$ and are polytypic forms of aluminium nitride in the AlN – C system.[91]

The compounds $Si_3Al_5N_5C_3$ and $Si_3Al_4N_4C_3$ with the wurtzite lattice[92,93] and $Si_3Al_5N_9$[94] are also known. However, despite the evident analogy with the structures in the Al – Si – C and Al – N – C systems, they are at present regarded as polytypes in the Si – Al – N – C system.

4. Boron carbide

Deformation polytypism is possible in boron carbide. This has been confirmed indirectly by data indicating the marked disordering in B_4C when the specimens are rubbed.[95] In the course of electron microscope studies of B_4C deformed at a high pressure and temperature (P = 7.7 GPa, T = 1800 °C) a similar disordering was also observed.[96] Furthermore, the formation of a mixture of MP was detected. It was established that the disordering is associated with the disperse twinning along one system of rhomohedral planes of the type $\{10\bar{1}1\}$.

5. Aluminium nitride

Among the nitrides, the most representative series of polytypes has been identified on the basis of aluminium nitride with the wurtzite structure (2H). AlN is represented by only this modification in the powders synthesised by various methods and in known polycrystalline materials of all types. The AlN sphalerite phase has not been detected (in contrast to its crystallographic analogues — SiC, ZnS, BN, lonsdaleite, *etc.*). However, the formation of the AlN phase with a NaCl-type face-centred cubic lattice in microvolumes has been established. It is segregated (in the form of needles, plates with a rectangular cross-section) when nitrogenated iron silicide is annealed. Its unit cell parameter is in this case a = 4.10 Å On heating above 600 °C, this phase is converted into the 2H form.[97] The face-centred cubic lattice of AlN may be formed from the 2H phase on application of high pressures in the course of static[98] and impact[99] compression. It has been noted[100] that the transition of AlN to the metallic state is possible at 90 GPa.

a. The Al – N – C system

The phenomenon of polytypism in aluminium nitride was first observed in the Al – N – C system in an X-ray study of single crystal specimens.[101] The latter were obtained by recrystallising AlN *via* the gas phase at T > 2000 °C in a graphite crucible. The polytypes were identified in this case in the form of a series of carbonitride phases differing in their space groups (Table 2). These phases have been described[91] as members of the $(AlN)_nAl_4C_3$ AlC series (n = 1 – 6) — with the AlN and Al_4C_3 extreme members of the series. It was postulated that the structure of the carbonitrides can be represented as the combination of three types of blocks: $[AlN]_n$, $[Al_2C_2]_n$, and $[Al_2C]_n$. For example, the rhombohedral structure can be accordingly described by a set of blocks in the following sequence: $([Al_2C_2]_n[AlN]_n[AlN]_n[Al_2C]_n$. $.[AlN]_{n[AlN]n})_3$. This representation of the structure of the carbonitrides was later confirmed by the fact that the calculated (according to the model) and experimental unit cell parameters a and c agreed. The carbonitrides have also been described[91] as multilayer structures in terms of Zhdanov's symbols (Table 2). The compositions Al_4C_3 and Al_5C_3N correspond to the 9R[88] and 8H[102] polytypes. The latter polytype is analogous to the 8H polytype in the Si – Al – O – N system.[102] The analogy consists in the fact that the carbon atom substituting nitrogen in the case of the Al – N – C system in four nonmetallic layers has a coordination number of 6, whilst other nonmetallic atoms are located in distorted tetrahedra between octahedral layers.

Hitherto the communications of Jeffrey and Wu[91,101] are the only ones in which the detection of multilayer structures in the AlN – C system has been reported.

b. The Al – N – O system

The polytype formation processes in AlN have been investigated in detail in a study of polycrystalline materials in the $AlN - Al_2O_3$, $AlN - SiO_2$, $Si_3N_4 - Al_2O_3 - AlN$, and $Si_3N_4 - Al_2O_3 - AlN - SiO_2$ systems. 2H AlN – O single crystals have been investigated only by

Table 2. Characteristics of the aluminium carbonitrides $(AlN)_nAl_4C_3$ with n = 0 – 6 which are multilayer structures in the AlN – C system.[91,101]

System	Space group	A	B	c/a	l/Å
Al_4C_3	$R\bar{3}m$	[13]	0012	7.474	2.074
Al_5C_3N	$P6mc$	[113]	0013	6.005	2.167
$Al_6C_3N_2$	$R\bar{3}m$	[1113]	0018	12.33	2.224
$Al_7C_3N_3$	$P6mc$	[11113]	0014	9.826	2.264
$Al_8C_3N_4$	$R\bar{3}m$	[111113]	0024	17.15	2.295
$Al_9C_3N_5$ [a]	$P6mc$	–	(0018)	(13.04)	(2.316)
$Al_{10}C_3N_6$ [a]	$R\bar{3}m$	–	(0030)	(21.97)	(2.333)

Note. The following designations have been adopted: A = packing sequence of the metal layers (Zhdanov's symbols are used); B = intence reflection in the 00l row; l = interlayer distance. [a] Hypothetical phases.

Bartram and Slack.[103] It has been reliably established that the polytypes in such materials are formed on the basis of the AlN phase with the wurtzite structure and they are therefore referred to as the wurtzite polytypes. However, they are frequently referred to as sialone (in the Si–Al–O–N system) and oxynitride (in the Al–N–O system) polytypes. Evidently these names of the polytypes lack significance since sialones are solid solutions of aluminium and oxygen in the Si_3N_4 lattice of the phenakite type, while aluminium oxynitrides are compounds with a cubic spinel-type lattice.

Three kinds of sialones are known. The phases formed in the region located along the Si_3N_4–$AlN \cdot Al_2O_3$ line (Fig. 4), for a fixed cation/anion ratio (M/X, where M = Al, Si and X = N, O) of 3/4, are described by the general formula $Si_{6-x}Al_xO_xN_{8-x}$ (with $x \leqslant 4.2$) and are referred to as β′-sialones.[104] These phases have a β-Si_3N_4 lattice. For $x < 0.4$ and the ratio M/X = 2/3, phases with the orthorhombic lattice characteristic of Si_2ON_2, are formed. They are described by the general formula $Si_{2-x}Al_xO_{2-x}N_{1+x}$ and are called O′-sialones.[104, 105] Both kinds of sialones are formed on the basis of the β-Si_3N_4 lattice. α-Sialones are formed in the M–Si–Al–O–N (M = Li, Mg, Ca, Y, V, Nd, La) systems on the basis of the α-Si_3N_4 lattice. They are described by the general formula $M_x(Si,Al)_{12}(N,O)_{16}$ $(0 \leqslant x \leqslant 2)$. The above metals M stabilise the Si_3N_4 α-phase.[106, 107]

Aluminium oxynitrides with a spinel lattice are formed when the AlN content is in the range from ~45 mol.% to 25 mol.%.[108] Since the spinel has the formula AlON, it contains ~34.5 mol.% of AlN.[109] In the literature, the spinel is designated as AlON but it is also possible to encounter the term 'nitrogen-stabilised aluminium oxide'. The nonstoichiometric spinel $9Al_2O_3 \cdot AlN$, for which there is a possibility of the formation of superstructures, is known.[110] The spinel Al_2O_3N is regarded as ideal. It may be obtained when the structural vacancies in Al_3O_3 are completely filled with nitrogen.[109] The phases in the AlN–Al_2O_3 system are formed by the reaction:[103]

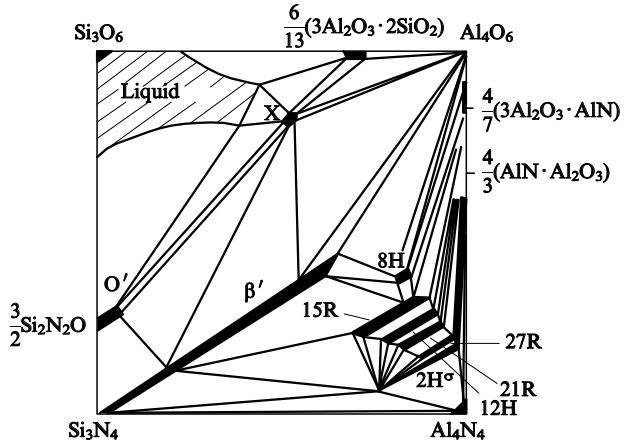


Figure 4. The isothermal section through the Si–Al–O–N diagram at 1750 °C.[112]

$$3zAlN + (1-z)Al_2O_3 \longrightarrow Al_{(z+2)}N_{3z}O_{(3-3z)}$$

(this is pure AlN for $z = 1$ and pure Al_2O_3 for $z = 0$). A whole series of intermediate phases differing in the value of z have been noted. The range $0.889 > z > 0.25$ is characteristic of the oxynitride phases.

The communication of Lejus[111] about the formation of polytypes in the AlN–Al_2O_3 system must be regarded as the first in which a new phase was detected. Later this phase was identified[112] as the 21R AlN polytype. Japanese investigators detected the 2H AlN–O solid solution (the authors called it the 2H pseudopolytype) and the 27R, 16H, 21R, and 12H polytypes in a material based on AlN (the Al_2O_3 content, was up to 12.3%).[113] Communications about the identification of the 20H and 27R polytypes[93] and the 12H, 27R, and 21R polytypes[114] by X-ray diffraction appeared almost simultaneously. In the first case, they were detected in a study of the single crystals obtained in the course of the resublimation of AlN at $T \simeq 2200$ °C in N_2 + 5% H_2, whilst in the second they were detected in a study of a polycrystalline composition having the formula $5AlN \cdot 9Al_2O_3$. In the latter case, they were detected in the range of compositions where a liquid phase is formed in the Al–O–N system.

Kurdyumov *et al.*[115] reported the formation of a 165R polytype on sintering a highly disperse AlN powder obtained by plasmachemical synthesis and containing ~2 mass% of oxygen. This polytype was detected in a 2H AlN grain in the form of a lamellar interlayer not containing other polytypes (Fig. 2).

In the course of an electron microscope study of a material having the composition AlN–Al_2O_3, Krishnan *et al.*[116] identified the 27R, 16H, and 32H polytypes; they observed the last polytype for the first time. In similar studies of a material obtained from AlN powder contaminated by oxygen as the accompanying impurity, the 33R and 20H polytypes were identified.[117] According to the communication of Youngman and Harris,[118] the 51R polytype, containing 6.6 at.% of oxygen, is formed in the AlN–O system. In the presence of MgO in this system, the formation of the 27R and 21R polytypes was discovered.[119]

Schuster[120] proposed a AlN–Al_2O_3 phase diagram based on the revised data of McCauley and Cowin[114] in which the tentative regions corresponding to the formation of the 12H, 27R, and 21R polytypes were identified (Fig. 5).

c. The Si–Al–N–O system

The AlN polytypes were first observed as new phases in the Si_3N_4–AlN–Al_2O_3–SiO_2 system by Gauckler *et al.*[104] and Jack[121] in the range of compositions with a high AlN content. These phases were represented[104] as Si–Al–O–N chemical compounds differing in the content of cations and anions. It was established by subsequent X-ray studies[122] that all the new phases observed have a wurtzite type lattice and can be described in terms of Ramsdell's symbols as multilayer structures (polytypes based on the 2H AlN lattice) (Table 3). Depending on the number of layers (n) in the polytypes, their parameters c are described by the following equations:[112]

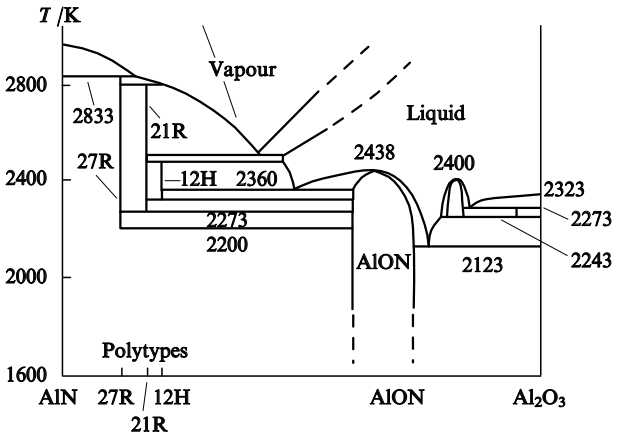


Figure 5. The AlN–Al_2O_3 phase diagram with identification of the regions corresponding to the formation of the AlN polytypes.[120]

$$c_R = (n-3)\left(\frac{c}{2}\right)_{AlN} + 3(4.014)\,,$$

$$c_H = (n-2)\left(\frac{c}{2}\right)_{AlN} + 2(4.014)\,.$$

Table 3. Characteristics of the identified polytypes in the Si–Al–O–N system.

Polytype	M/X	a /Å	c /Å	c/n /Å	Ref.
8H	4/5	2.988	23.02	2.88	112
15R	5/6	3.010	41.81	2.79	112
12H	6/7	3.029	32.91	2.74	112
21R	7/8	3.048	57.19	2.72	112
27R	9/10	3.059	71.98	2.67	112
33R	11/12	–	86.46	2.62	122
24H	12/13	–	101.4	–	122
39R	13/14	–	–	–	122
$2H^{\delta}$ (see [a])	–	3.079	~5.30	2.65	112
2H	1/1	3.114	4.986	2.49	112

[a] $2H^{\delta}$ = solid solution of oxygen and silicon in 2H AlN.

A Si–Al–O–N phase diagram, in which the regions corresponding to the formation of AlN polytypes (or X-phases) [104] were identified, has also been put forward (Fig. 4).[112] This diagram, confirmed in a further study of the system, is nowadays widely known. According to the diagram, the polytypes are in the region with a high AlN content along a line corresponding to a constant cation/anion ratio. The polytypes described in the above study [112] were identified by electron microscopy [123] in a study of material having the initial composition $Si_3N_4 + AlN + Al_2O_3$ hot-pressed at 1600–1750 °C. Later in the course of similar studies of material obtained by sintering $AlN + SiO_2$, the 33R, 24H, and 39R polytypes were discovered and their characteristics were determined (Table 3).[122] Overall, the composition of the polytypes in the Si–Al–O–N system is described by the general formula $Al_{x+y}Si_{6-y}O_xN_{8-x+y}$, where $x = 4$ and $y = 2n$ (n is an integer varying from 0 to 10).

Polytypes have also been observed in the M–Si–Al–O–N systems. The 12H, 15R, 21R, and 20H polytypes were identified by X-ray diffraction in hot-pressed material based on the initial composition $MgO + Al_2O_3 + Si_3N_4$.[112] Subsequently the 12H, 15R, 7(21)R, and 8(16)H polytypes were found by electron microscopy in material of the same composition and it was established that they differ in the amounts of Mg–Al and Si–O.[124] According to the data of Kuang *et al.*,[124] the 12H polytype with the ratios Mg : Al : Si = 1 : 0.3 : 1.2 is formed in the Si–Al–O–N system in combination with MgO. It is also produced at 1400 °C and is stable up to the temperature of the appearance of the new phase.

The 15R polytype has been observed in the Si–Al–O–N system with lithium [112] and the 33R polytype was found in the same system with calcium.[125] Polytypes have been noted also in the system with yttrium. For example, the 15R and 8H polytypes were identified by Ekstrom *et al.*[126] at a sintering temperature less than 1800 °C, while the 27R polytype was identified by Topfer and Muller.[127]

A characteristic feature of the polytype formation in the Y–Al–Si–O–N system must be pointed out.[128] The 27R polytype was formed in specimens having the initial composition $AlN + SiO_2$ at 1700–1800 °C; when Y_2O_3 was introduced into this composition, the amount of the polytype diminished. In the course of the subsequent annealing of a mixture of ground specimens having the first composition to which Y_2O_3 had been added, the content of the polytype fell, starting already at 1400 °C, whilst at higher temperatures it vanished altogether. This feature is due to the formation of oxygen-rich stable phases in the $Al_2O_3–Y_2O_3$ system above 1250 °C. This in fact induces the binding of the oxygen present in the initial $AlN + SiO_2$ system and also contained in specimens in which the 27R polytype is present after sintering.

d. Microstructural features of the formation of polytypes

The polytype formation in the Al–O–N and Si–Al–O–N systems is characterised by the following general features.

The formation of polytypes is observed in most cases above 1700 °C, although there have been reports of their appearance in the Si–Al–O–N system at 1400 °C [129] and 1600 °C.[130] Polytypes are formed in materials obtained by sintering porous pressed materials produced by the usual hot pressing and isostatic pressing procedures. In the treatment of materials at high pressures and temperatures (starting from 2 GPa at 1700–1800 °C), polytypes are not formed.

In the first stage, polytypes are always formed within the grains. At 1700–1800 °C, the polytypes are in most cases produced in the form of lamellar interlayers in the grains (Fig. 2), whilst at higher sintering temperatures individual grains with the same morphology are formed in the materials.[85] When highly disperse AlN powders, obtained by plasmachemical synthesis, are sintered, thin lamellar interlayers may be formed within the limits of the entire grain. In rare instances, a polytype with the same number of layers is formed within a single grain.[115] A typical example is a mixture of polytypes with different numbers of layers combined with a solid solution of oxygen or of oxygen and silicon in AlN ($2H^{\delta}$). In the lamellar interlayers, they are usually present in the form of blocks of different thickness grown together, coherently *via* the (0001) planes, *i.e.* they actually constitute a composite modulated structure. The electron microdiffraction patterns of sections of the $(11\bar{2}0)$ type through the grains show a series of non-systematic point reflections in the 00*l* and *h*0*l* rows (Fig. 6). In the course of the recrystallisation growth of the grains, the polytypic composition along the length of both the MP interlayer and the individual grains having the same composition remains unchanged. All the variants of the development of the granular structure are presented in Fig. 3. In the course of the growth of the grains, the fraction of MP in the polycrystalline material increases as a result of the diffusional rearrangement, of the 2H phase in the MP within the migrating boundary. It is significant that in this instance the reverse transformation 2H → MP may also take place. Reversible grain → boundary polytypic transitions also occur in SiC-based materials.

An unusual instance of polytype formation has been noted [131] in the Si_3N_4–SiC system to which Er_2O_3 and AlN had been added: the 21R polytype ($SiAl_6O_2N_6$) crystallises epitaxially on the basal surface of the 6H SiC plates.

There is no information about the regions of stability of the AlN polytypes in the Al–O–N and Si–Al–O–N systems. Data on the tentative regions in which three polytypes are located on the $AlN–Al_2O_3$ phase diagrams have been published in only one study (Fig. 5).[120] However, careful investigations on these lines have not been carried out. It has been established reliably that, as the oxygen content in the initial AlN decreases, the number of layers in the polytypes rises. The longest-period 51R polytype has now been identified: it has a 17-layer sequence repeated three times; its oxygen content is 6.6 at.%.[118] The 165R polytype identified by Kurdyumov *et al.*[115] most probably consists of

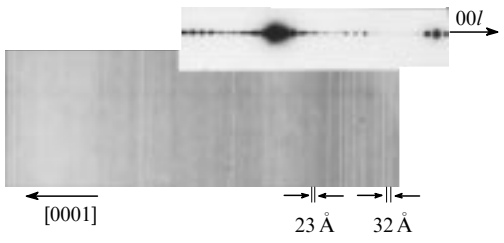


Figure 6. Interference pattern in the resolution of the 2H AlNO planes (0001) in an oxygen-enriched interlayer and an electron microdiffraction pattern [the $(11\bar{2}0)$ section].

blocks of short-period structures, as is usually observed for SiC polytypes with a large number of layers (126R[80] and 201R[81]). It has also been established[132] that at high pressures and temperatures (8–10 GPa and > 2200 °C) the multilayer polytypes in the AlN–O system are unstable: they undergo a transition to the 2H phase and the cubic aluminium oxynitride.

e. Models of the structure of AlN polytypes

A model of the structure of the wurtzite AlN polytypes was first proposed by Jack.[112] As in the case of the polytypes in the AlN–C system,[91,101] it is based on the idea of the formation of multilayer structures from blocks of different chemical composition. The unit cell of each polytype contains n layers divided into blocks: two in the case of hexagonal and three in the case of rhombohedral symmetry. Each block consists in its turn of m layers. The number of layers in the hexagonal and rhombohedral polytypes is therefore represented as $n = 2m$ and $n = 3m$ respectively. One layer in each block contains an excess nonmetal atom, while the remaining layers are the basal (0001) 2H AlN layers. This means that the layer specified has the composition MX_2, in contrast to the composition MX of the basic structure. On these grounds, the composition of the polytypes is described by the general formula M_mX_{m+1}, where m is an integer; we have the ratio $M/X < 1$. Hence a difference between the chemical compositions of the polytypes is evident.

The formation of layers having the composition MX_2 is determined by the local change in the coordination number of aluminium from four (characteristic of the 2H structure) to six and is induced by the dissolution of oxygen in AlN.[112] The change in the packing sequence in the AlN polytypes is attributed to the number and periodicity of the disposition of the MX_2 layers containing Al atoms with a coordination number of six. It has been suggested that the latter is determined by the appearance of packing defects in the aluminium sublattice of 2H AlN (the change in the AB, AB alternation of aluminium atoms to ABC, ABC), induced by the localisation of the nonmetal atoms and hence by the decrease in the distance between them.

In the subsequent structural studies, data were obtained confirming the proposed model of the structure of polytypes. It has been established by electron microscopy[123] that the change in the periodicity of the polytypes in the Si–Al–O–N system is determined by the presence of planar two-layer defects along the basal planes. On the basis of X-ray studies of two polytypes (8H and 15R), it was concluded that they contain 2H AlN layers distributed periodically in the basal planes and containing aluminium surrounded by six oxygen atoms (AlO_6).[133] The calculated images for the 12H and 15R polytypes, taking into account the regular alternation of the octahedrally coordinated aluminium atoms, corresponded to the images obtained by convergent beam electron diffraction.[134]

On the basis of the ideas concerning multilayer structures in the AlN–C system developed by Jeffrey and Wu[91,101] and Thompson's data,[133] Bartram and Slack[103] and Krishnan *et al.*[116] suggested that the MX_2 layers in the polytypes of the Al–N–O system be regarded as α-Al_2O_3 interlayers with a thickness equal to the parameter c of the morphological cell of corundum (the parameter c of this cell is equal to half the parameter c of the structural cell). In this model, the experimental and calculated values of c for the 20H and 27R polytypes agree well. The experimental values were respectively 53.10 and 72.24 Å. In the calculations, account was taken of the determinations of the interlayer distance and of the range of the known values of c for the morphological cell of Al_2O_3. The following ranges of values of c (Å) were established: 50.92–53.58 for the 20H polytype and 68.77–72.76 for the 27R polytype.[103]

In later studies, new data were obtained concerning the nature of the planar oxygen-containing MX_2 layers (O-defects) in the basal planes of AlN and a series of structural models of their formation were proposed. According to Hagege *et al.*,[135] such layers represent a packing defect containing an octahedrally coordinated aluminium atom and arising with participation of vacancies generated on formation of the 2H AlN–O solid solution. It has been postulated[136] that the O-defects are antiphase domain boundaries and their thickness in the direction of the [0001] axis of AlN is 1/2 or 1/3 of the α-Al_2O_3 structural cell. Experimental studies established[137] that the defects are inversion domain boundaries (IDB) and that they contain lamellar formations enriched in oxygen.

According to the ideas of Harris *et al.*,[138] the logical sequence of the processes determining the formation of the O-defects is as follows. At an oxygen concentration less than 0.75 at.% in the 2H AlN–O solid solution the complexes $V_{Al} + O_N$, where V is a vacancy, are formed. It has been established experimentally that the formation of the complexes is accompanied by a decrease in the parameter c of 2H AlN and by the contraction of the lattice (Fig. 7). At higher oxygen concentrations, the mode of incorporation of oxygen into AlN changes (this is indicated by the restoration of the volume of the 2H lattice). It has been suggested[138] that in this case octahedral defects, the formation of which is accompanied by the annihilation of the aluminium vacancies, arise initially. A unit defect consists of a combination of an aluminium atom with six oxygen atoms. With increase in the oxygen concentration, such octahedral defects coalesce with formation of planar IDB, the regular disposition of which in the 2H lattice of AlN is in fact responsible for polytype formation.

A model of the structural rearrangement determining the formation of the O-defects has been proposed.[138] In this model, the development of a displacement process is postulated with a vector $\mathbf{R} = (1/3)\langle 10\bar{1}1\rangle$, which may be split into two components: $\mathbf{R} = (1/3)\langle 10\bar{1}0\rangle + (1/3)\langle 0001\rangle$. This model has been confirmed.[139] In later studies, it was demonstrated experimentally that the vector of the displacement of the O-defect is $\mathbf{R} = (1/3)\langle 10\bar{1}0\rangle + 0.387\langle 0001\rangle$ and that this is close to the calculated value $\mathbf{R} = (1/3)\langle 10\bar{1}0\rangle + 0.394\langle 0001\rangle$.

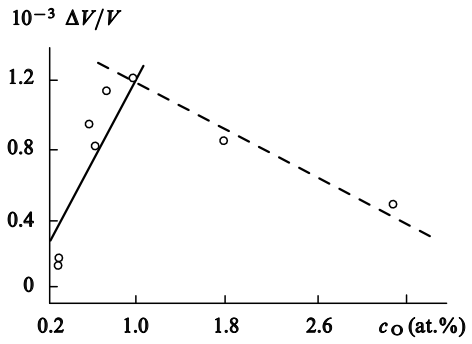


Figure 7. Variation of the volume ($\Delta V/V$) of the AlN unit cell with increase in the concentration of dissolved oxygen.[138]

The ideas[138] concerning the formation of planar IDB described are known as Youngman's model of the defect. This model has been confirmed:[140] the experimental oxygen content in the IDB (amounting to 6.0 ± 0.8 mass %) is close to the value calculated (5.7 mass %) in accordance with Youngman's model. We may note that the principal postulate of Youngman's model — the change in the structural state of oxygen in 2H AlN–O with increase in its concentration — has been confirmed also by the results of the study of the structure of this solution in thin films.[141] It has been shown that the dissolution of oxygen in AlN with increase in concentration has three stages: I — complete dissolution; II — the formation of aluminium oxynitride; III — the formation of γ-Al_2O_3.

The nature of the periodic segregation of oxygen-containing basal layers in the 2H lattice and the mechanism of polytype formation in the 2H AlN–O solid solution were fully examined by the present authors in another communication.[142] This was based

on the results of a detailed study by transmission electron microscopy in combination with microdiffraction of the evolution of structural transformations in the 2H AlN–O and 2H AlN–O–Si solid solutions, starting with the stage involving the appearance of unit basal packing defects in the grains and ending with the formation of lamellar grains made up of a mixture of multilayer AlN polytypes.

f. The model of the formation of polytypes

The formation of polytypes as a result of the generation of O-defects in the AlN basal layers is associated with two stages in the decomposition of the 2H AlN–O solid solution, which occurs above 1700 °C.[142] According to experimental data, the first stage is the isostructural separation into layers, leading to the segregation in the single-crystal grains of oxygen-enriched lamellar interlayers, along the (0001) plane. A single plate is usually generated in the grain, intersecting it from boundary to boundary; its thickness in the [0001] direction is 0.5–1 μm (Fig. 2). The change in the oxygen concentration of the enriched lamellar interlayer in the [0001] direction is nonperiodic, because separation into layers occurs in each instant at a different concentration in the solid solution, *i.e.* a set of zones with different concentrations is formed in the interlayer.

The separation of the 2H AlN–O solid solution into layers occurs *via* the ascending diffusion mechanism (*i.e.* $\bar{D} < 0$, where $\bar{D}$ is the diffusion coefficient), caused by the sharp decrease in the energy of the basal packing defects within the grains of the 2H AlN–O solid solution.[142] The decrease in energy is induced by the localisation of oxygen (Suzuki segregation) in the region of the packing defect. The occurrence of such segregations determines the appearance of a stress gradient as the driving force of ascending diffusion. The latter is due to the following causes.

Taking into account the conditions for isomorphous heterovalent substitution,[83] the 2H AlNO formation reaction is as follows:

$$3Al_{Al}^{3+} + 3N_N^{3-} \xrightarrow{O} 2Al_{Al}^{3+} + 3O_N^{2-} + V_{Al}\,.$$

The oxygen in such a solid solution exists in the form of the complexes $2Al_{Al}^{3+} + 3O_N^{2-} + V_{Al}$. The occurrence of oxygen segregations on the packing defect is associated with the migration of such complexes, *i.e.* with the simultaneous diffusion of aluminium along the cationic sublattice and of oxygen along the anionic sublattice, which means that it is associated with the constant appearance of a compressive stress (as a result of the presence of vacancies) in the vicinity of the packing defect. The magnitude of such stresses ε is proportional to the concentration of vacancies:[143]

$$\varepsilon = \sum \beta_i N_i\,,$$

where β_i are deformation constants proportional to the difference between the ionic radii of the defects and the matrix and N_i is the concentration of point defects. Under the conditions of ascending diffusion under the influence of the stress gradient, atoms with a larger radius should tend to migrate into the stretched regions, while those with a smaller radius should tend to move into the compressed regions.[144] The latter (bearing in mind that $r_O < r_N$, where r represents the size of the atom) occurs in the case of 2H AlN–O and is responsible for the formation of oxygen-enriched layers along the planes containing the packing defect.

The second stage of the decomposition of the solid solution occurs in the oxygen-enriched interlayer produced on isomorphous separation into layers. It is determined by the sequence of structural transformations, the development of which is in fact responsible for the generation of basal O-defects and hence the formation of polytypes. These transformations occur in three stages.

1. The formation of oxygen clusters. The presence of such clusters is confirmed by the geometry of the reflections on the electron microdiffraction patterns from enriched interlayers (Fig. 8). The clusters are formed already in the process involving the separation of the solid solution into layers and consist of the basal layers of AlN enriched to different extents by oxygen substituting the nitrogen atoms. It is believed that[145] the establishment of order in the system occurs as a result of the growth of some clusters and the disappearance of others. There is a definite correlation distance between the former clusters (which is due to the need to achieve the condition for the minimisation of their interaction energy). The minimisation condition determines also the form of the clusters, namely as Al–O basal layers. According to the ideas developed by Khachaturyan,[146] in solid solutions with a negative anisotropy parameter, formations in the form of plates arranged in the direction of the minimum modulus of elasticity have the minimum elastic energy. For AlN, the anisotropy parameter is −0.07. Evidently the cluster ordering process takes place, like the separation of the solid solution into layers, *via* the ascending diffusion mechanism. As noted above, a set of concentration zones are generated in the oxygen-enriched interlayers. Within the limits of each zone, clusters with a definite correlation distance are produced.

2. The formation of three-layer oxygen-containing defects from the clusters. This process is determined by the ordering of the vacancies in the AlN cationic lattice, inevitably accompanying the ordering of the clusters formed from associated species having the composition $(2Al_{Al}^{3+} + 3O_N^{2-} + V_{Al})$. One of the aluminium vacancies is formed after the substitution of three nitrogen atoms by oxygen, which means that the growth of clusters leads to the formation of three-layer defects in the (0001) planes — two oxygen-containing Al–O basal layers separated by a V_{Al}–O layer. The segregation of such defects in the oxygen-enriched zone occurs with a periodicity specified by the motif in the disposition of the clusters. The presence of empty sublayers (V_{Al}) in the defects should lead to the appearance of directed stresses. This has in fact been confirmed by microdiffraction studies (Fig. 8 *d*).

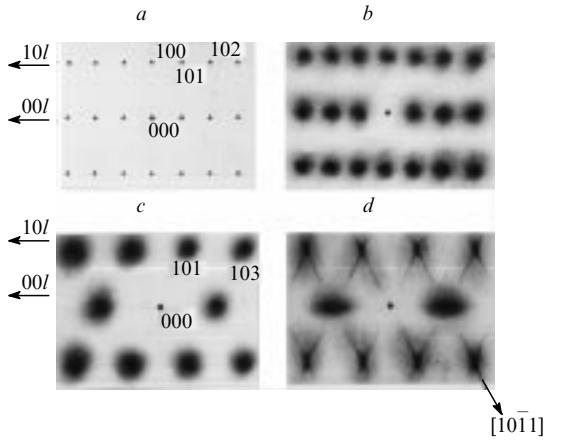


Figure 8. Schematic illustration of the electron microdiffraction pattern of the (11$\bar{2}$0) section through a grain of the initial 2H AlN–O solid solution (*a*) and of the interlayer formed as a result of layer formation (*b*–*d*); (*b*) and (*c*) nonordered cluster state; (*d*) state with directed stresses.

3. The crystallographic shifts along the (0001) plane in three-layer defects. Such shifts lead to the exclusion of the vacancy sublayer and to a local rearrangement, of the 2H lattice in the defect into a fragment of the lattice of the α-Al_2O_3 segregation phase. The shifts develop with a periodicity specified by the motif in the arrangement of the defects. The regular formation of layers of the segregation phase modulates the basic 2H structure to give a structure with a different phase composition and a different unit cell parameter c. Such structures actually represent polytypes.

The possible mechanism of the rearrangement of the three-layer defects to the Al–O segregation phase in the 2H AlN lattice is as follows: The bonds between the atoms in the three-layer defect differ from those in the 2H structure, because the appearance of even one vacancy V_{Al} on formation of the solid solution

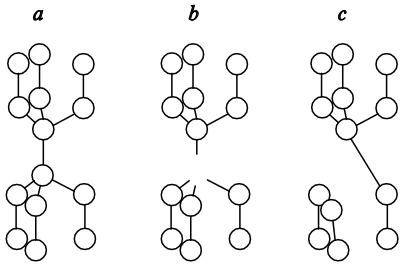


Figure 9. Schematic illustration of the single bond between diatomic layers in the 2H lattice with formation of aluminium vacancies [the $(11\bar{2}0)$ section]; (*a*) normal unit; (*b*) formation of vacancies; (*c*) relaxation of the bond on formation of vacancies.

inevitably leads to the appearance of the O–O bond. This can be seen in Fig. 9, which represents a schematic arrangement of the atoms in a unit fragment of the 2H structure in the $(11\bar{2}0)$ section. The appearance of a three-layer defect with a V_{Al} sublayer should lead to the formation of the O–O bond between the Al–O layers. The direction of this bond is parallel to the plane of the pyramid of the tetrahedron of the first kind (Fig. 10). The characteristic features of the structure of the electron microdiffraction pattern, of the $(11\bar{2}0)$ sections of the interlayers containing the solid solution and multilayer AlN polytypes, namely the presence of diffuse rows in directions of the type $[10\bar{1}1]$ (Fig. 8 *d*), may be regarded as confirmation of the formation of such a bond. Rows of this kind are known[146, 147] to be a sign of the generation of directional stresses.

On formation of a continuous layer of vacancies, their collection into a loop is inevitable, which implies the formation of a chemical packing defect.[148] Such defects are characteristic of layered nonstoichiometric compounds, for example Sb_2Te_3. In the three-layer defects in the AlN structure which we considered, the vacancies are located only in one sublayer of the diatomic layers. They then induce the appearance of directed stresses. Such stresses

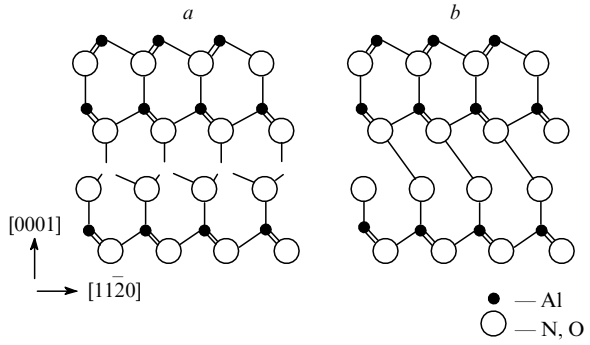


Figure 10. Schematic illustration of the formation of the O–O bond in a three-layer AlN defect formed following the ordering of the aluminium vacancies [the $(11\bar{2}0)$ section]; (*a*) appearance of vacancies in the layer; (*b*) relaxation of the bond following the appearance of vacancies.

in the 2H lattice should promote a shift along the basal plane. According to the data of Funk and Sochel,[149] this type of shift occurs on disorientation (α) of the [0001] axis and the directions in which the stresses act are in the range $0 < \alpha < 90°$. In our case, the angle between the direction of type $[10\bar{1}1]$ and the [0001] axis is 32°. The occurrence of such a shift promotes the elimination of the V_{Al} sublayer and may be classified in the development of the Wadsley crystallographic shift.[150]

The elimination of the V_{Al} sublayer in the defect may be represented by two elementary steps involving the migrations of aluminium atoms under the influence of directed stresses (Fig. 11 *a*). The first involves the migration of the aluminium atoms from layer *I* (Al–O) to layer *II* (V_{Al}–O). Formally, this implies the formation of a packing defect, in the hexagonal close-packed aluminium sublattice, which is accompanied by a local change in the alternation of the atoms from AB AB... to ABC ABC.... The second step involves the migration of aluminium atoms in layer *III* (Al–O) over an interatomic distance. In this case, there is a shift in the (0001) plane. Such migrations are responsible for the change in the coordination number of aluminium from four to six and hence for the addition of oxygen atoms from layer *II* (V_{Al-O}). Formally, this can be represented as the combination of four tetrahedra (as elements of the wurtzite lattice) to form an octahedron which is an element of the structure of α-Al_2O_3. Comparison of Fig. 11 *b* with Fig. 12 shows that the disposition of aluminium and oxygen atoms in the lattice fragment, formed as a result, of the migrations indicated corresponds to their positions in two layers of the unit cell of α-Al_2O_3.[151] A distinctive feature of the structure of such a fragment compared with that of α-Al_2O_3 is that an aluminium atom from one layer is bound to five oxygen atoms and a nitrogen atom, *i.e.* it belongs simultaneously to the 2H lattice and the Al_2O_3 segregation phase. This also applies to the oxygen atom from the second layer because it is bound to an aluminium atom belonging to 2H AlN.

The thickness of two Al–O layers of the segregation phase is $c/4 = 3.24$ Å (c is the cell parameter) (Fig. 12). We may note that, according to the data of Bartram and Slack,[103] the quantity $c/4$ may vary from 2.58 to 3.25 Å. The estimation of the thickness of the layers of this phase in the 2H AlN lattice, taking into account, the distance between the aluminium and nitrogen atoms, yields 3.01 Å (the distance between diatomic layers in the direction of the c axis is 1.97 Å, whilst that between the atoms in the diatomic layer is 0.52 Å). This indicates the possibility of the formation of a fragment of the α-Al_2O_3 lattice structure in the form of two layers in the 2H AlN lattice. The segregation of AlO in the α-form is determined by the similarity of the ratios c/a in AlN and in this form ($c/a = 1.6$ in the former case and 1.58 in the latter) and also of the distances between the atoms in them: the distances between close unlike atoms are 1.97 and 1.86 Å in Al_2O_3 and 1.917 and 1.885 Å in AlN. The packing of the chains of oxygen atoms in the basal layers of the α-Al_2O_3 lattice is close to the packing of the nitrogen atoms in the AlN lattice. The principal difference between these structures is associated with the coordination number and also

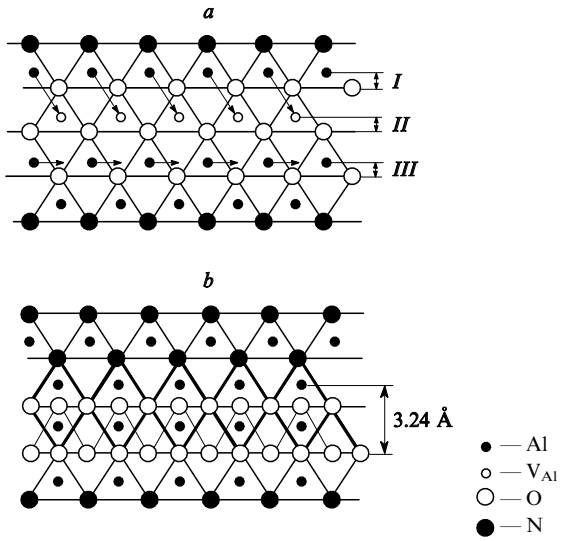


Figure 11. Schematic illustration of the migration of aluminium atoms in a three-layer defect on elimination of a sublayer of aluminium vacancies (*a*) and the disposition of the aluminium and oxygen atoms in the two-layer segregation generated after the elimination of the above sublayer (*b*) [the $(11\bar{2}0)$ section].

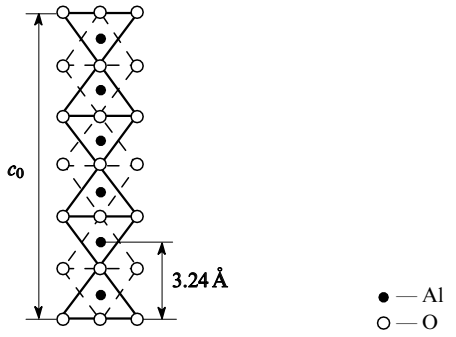


Figure 12. Schematic illustration of the disposition of aluminium and oxygen atoms in Al_2O_3 [the (11$\bar{2}$0) section].

with the disposition of the central aluminium atom: it has a coordination number of 6 and is located in an octahedral environment in an α-Al_2O_3, whereas in AlN a coordination number of 4 is characteristic of this atom and the latter is located in a tetrahedral environment. Thus the rearrangement in the three-layer defect on development of the shift ensures a change in the location and hence in the coordination number of aluminium.

The lattice parameters of 2H AlN and α-Al_2O_3 in the coupling plane differ appreciably (a = 3.11 Å for AlN and 4.748 Å for Al_2O_3), so that the following question arises inevitably: is the formation of α-Al_2O_3 layers in the 2H AlN lattice possible? From a formal point, of view, the noncorrespondence stress in their coupling plane, estimated from the relation

$$\sigma = \frac{E}{1-v}\,\frac{a_{Al_2O_3} - a_{AlN}}{a_{cp}},$$

(E = 350 GPa is Young's modulus and v = 0.18 is the Poisson coefficient) should be 178 GPa. This greatly exceeds the theoretical limiting strength for a $\mu/10$ shear (the modulus of shear is μ = 30 [152]) and 137 Gpa.[153] However, according to Khachaturyan's ideas,[146] in the case where a second phase is segregated in the solid solution in the form of thin plates for a small d/l ratio (d is the thickness and l the length of the plates), the interphase stresses should be extremely insignificant. In our case, this ratio is of the order of 10^{-4}. We may note that the deposition of AlN layers on α-Al_2O_3 supports with epitaxial intergrowth along the basal planes has been observed by a number of investigators, for example by Dobrynin *et al*.[100]

g. Calculation of the parameter c for the polytypes in the Al – N – O and Si – Al – N – O systems

According to modern ideas, the structural elements of the classical polytypes (SiC, ZnS, *etc*.) with hexagonal and rhombohedral symmetries consist respectively of two and three symmetrically disposed blocks with one structural packing defect. According to Oleinik and Shevchenko,[142] in the AlN polytypes there should be for each block, not a packing defect, but a two-layer segregation of Al_2O_3 with a thickness $c/4$. The number of 2H AlN layers per structural cell of the polytype can be determined by subtracting from the total number of layers the number of two-layer Al_2O_3 fragments, which is four for polytypes with hexagonal symmetry and six for those with rhombohedral symmetry. For example, in a 20-layer hexagonal polytype containing four Al_2O_3 fragments (with a thickness $c/4$), there should be 16 2H AlN layers. The compositions (corresponding to the morphological cell, *i.e*. to one block) of the polytypes have been determined by means of this approach with the increase in the number of AlN layers in the formula unit from 1 to 15. The parameters c of these polytypes were calculated from the compositions and dimensions (the parameter d_{002}) of unit AlN and Al_2O_3 layers in the direction of the [0001] axis. This quantity is 2.49 Å for AlN and is equal to the thickness of the two-layer lattice fragment, *i.e*. to 3.24 Å, for Al_2O_3. The above characteristics of the polytypes are presented in Table 4. Evidently all known polytypes fit within the above sequence. The calculated values of c agree well with the experimental results for certain polytypes.

Table 4. Characteristics of the polytypes in the AlN – Al – O system.

Polytype [a]	M/X	Composition	No. of layers		c /Å	
			AlN	Al_2O_3	I [142]	II [116]
9R	3/4	Al_3O_3N, $AlN \cdot Al_2O_3$	3	6	26.91	–
8H	4/5	$Al_4O_3N_2$, $2AlN \cdot Al_2O_3$	4	4	22.92	–
15R	5/6	$Al_5O_3N_3$, $3AlN \cdot Al_2O_3$	9	6	41.85	–
12H	6/7	$Al_6O_3N_4$, $4AlN \cdot Al_2O_3$	8	4	32.88	–
21R	7/8	$Al_7O_3N_5$ $5AlN \cdot Al_2O_3$	15	6	56.81	–
16H	8/9	$Al_8O_3N_6$, $6AlN \cdot Al_2O_3$	12	4	42.84	40.7
27R	9/10	$Al_9O_3N_7$, $7AlN \cdot Al_2O_3$	21	6	71.75	72.0
20H	10/11	$Al_{10}O_3N_8$, $8AlN \cdot Al_2O_3$	16	4	52.8	53.1 [b]
33R	11/12	$Al_{11}O_3N_9$, $9AlN \cdot Al_2O_3$	27	6	86.89	–
24H	12/13	$Al_{12}O_3N_{10}$, $10AlN \cdot Al_2O_3$	20	4	62.76	–
39R	13/14	$Al_{13}O_3N_{11}$, $11AlN \cdot Al_2O_3$	33	6	101.61	–
28H	14/15	$Al_{14}O_3N_{12}$, $12AlN \cdot Al_2O_3$	24	4	70.72	–
45R	15/16	$Al_{15}O_3N_{13}$, $13AlN \cdot Al_2O_3$	39	6	116.55	–
32H	16/17	$Al_{16}O_3N_{14}$, $14AlN \cdot Al_2O_3$	28	4	82.68	82.82
51R	17/18	$Al_{17}O_3N_{15}$, $15AlN \cdot Al_2O_3$	45	6	131.49	–

Note. The following designation have been adopted: I — calculations; II — experiment. [a] Polytypes the desighation of which are printed bold were established experimentally, whilst the remaining ones are hypothetical. [b] Data of Bartam and Slack.[103]

The polytypes in the Al_2O_3 – AlN system can be represented by the general formula $zAlN \cdot Al_2O_3$, where z is any integer. The number of layers in the polytypes with rhombohedral (n_R) and hexagonal (n_H) symmetries in the sequence deduced above (Table 4) is described by the following relations:

$$n_R = 9 + 6n,$$

$$n_H = 8 + 4n,$$

where n is an integer: $0 < n < 7$ in the former case and $0 < n < 6$ in the latter.

The proposed mechanism [142] of polytype formation in the 2H AlN – O solid solution can operate in the four-component Al – N – Si – O solid solution. The following considerations lead to this conclusion.

When the above solid solution is produced, the positively charged centres ($Si^{4+} - N^{3-}$) and ($Al^{3+} - O^{2-}$) are generated. The electroneutrality of the lattice can be ensured, as in the case of the 2H AlN – O solid solution, by the formation of the associated species $Si^{4+} + Al^{3+} + 2O^{2-} + N^{3-} + V_{Al}$. The associated species of the system under consideration include two cations and three anions. This suggests that a similar segregation based on the clusters occurs in the system with silicon but differs in the formula

composition, which corresponds to the composition of the electrically neutral complexes, *i.e.* $AlSiNO_2$. The latter is a sialone phase. The existence of such phases with the composition $MSiNO_2$ (M = Ce, La, Y) has been reported,[154] but their structure has not been investigated. On the basis of conditions for isomorphous substitution in the Si–Al–O–N system, this phase can be represented as a solid solution of silicon and nitrogen in α-Al_2O_3. Consequently the thickness of the two-layer segregation with the composition $AlNSiO_2$ in the polytypes based on 2H AlN-SiO should be close to 3.24 Å, which is characteristic of the segregations in the 2H AlNO solid solution.

The thickness of the two-layer segregation in the polytypes of the AlN–SiO_2 system can be calculated with the aid of experimental parameters c for the known polytypes in this system using the following relation:[112]

$$(d_{002})_{AlNSiO_2} = \frac{c - v(d_{002})_{AlN}}{w},$$

where v and w are the numbers of AlN and $AlNSiO_2$ layers per unit cell. The calculated thickness of the $AlNSiO_2$ segregation is ~3.25 Å, *i.e.* is close to the thickness of the α-Al_2O_3 fragment in the polytypes of the AlN–Al_2O_3 system.

The formula compositions and the parameters c of various polytypes in the AlN–SiO_2 system have been calculated taking into account the composition and thickness of the segregation (3.25 Å) (Table 5). Evidently the calculated and experimental parameters are identical for the known polytypes.

The compositions of the 15R and 12H polytypes were identified as $Al_4O_2N_4Si$ and $Al_5O_2N_5Si$ respectively with the aid of X-ray dispersion-energetic spectroscopy and electron loss spectroscopy.[155] Overall, the polytypes in the AlN–SiO_2 system can be described by the general formula $Al_{x+y}Si_{6-x}O_xN_{8-x+y}$, where $x = 4$ and $y = 2n$ (n is an integer varying from 0 to 10).

Table 5. Characteristics of the polytypes in the AlN–SiO_2 system.

Polytype	M/X	Composition	x	y	No. of layers		c /Å	
					see [a]	see [b]	I	II
9R [c]	3/4	$Al_2SiN_2O_2$, $AlN(AlNSiO_2)$	4	0	3	6	26.97	—
8H	4/5	$Al_3SiN_3O_2$, $2AlN(AlNSiO_2)$	4	2	4	4	22.96	23.02
15R	5/6	$Al_4SiN_4O_2$, $3AlN(AlNSiO_2)$	4	4	9	6	41.91	41.81
12H	6/7	$Al_5SiN_5O_2$, $4AlN(AlNSiO_2)$	4	6	8	4	32.92	32.91
21R	7/8	$Al_6SiN_6O_2$, $5AlN(AlNSiO_2)$	4	8	15	6	56.85	57.19
16H [d]	8/9	$Al_7SiN_7O_2$, $6AlN(AlNSiO_2)$	4	10	12	4	42.88	—
27R	9/10	$Al_8SiN_8O_2$, $7AlN(AlNSiO_2)$	4	12	21	6	71.79	71.98
20H [d]	10/11	$Al_9SiN_9O_2$, $8AlN(AlNSiO_2)$	4	14	16	4	52.84	—
33R	11/12	$Al_{10}SiN_{10}O_2$, $9AlN(AlNSiO_2)$	4	16	27	6	86.73	86.46
24H	12/13	$Al_{11}SiN_{11}O_2$, $10AlN(AlNSiO_2)$	4	18	20	4	62.80	—
39R	13/14	$Al_{12}SiN_{12}O_2$, $11AlN(AlNSiO_2)$	4	20	33	6	101.67	101.4

Note. The following designations have been adopted: I — calculation,[142] II — experiment.[112, 122] [a] No. of AlN layers. [b] No. of $AlNSiO_2$ layers. [c] Hypothetical polytype. [d] Polytype identified in the Mg–Si–Al–O–N system.[119]

h. The role of oxygen in AlN polytype formation

The scheme for the structural transformations in 2H AlN–O examined above suggests that the polytype formation in AlN is determined by the regular endotaxy of the Al_2O_3 layers in the 2H matrix in the direction [0001], while the polytypes are intergrowth microstructures. The latter are characterised by the fact that the intergrowth phases have a common cationic sublattice, but in one of them the sublattice atoms are located in tetrahedral vacancies (AlN), whilst in the other they are in octahedral vacancies (Al_2O_3). Overall, the structural changes in the 2H AlN–O solid solution, which determine polytype formation, are analogous to the changes characteristic of the ageing of solid alloys. The latter is accompanied by a stage of separation into layers and the subsequent stage involving the local formation of the lattice of the segregation phase.[156] Different AlN polytypes can be represented by a series of consecutive stoichiometric ordered phases.

The mechanism of the AlN polytype formation described for systems with only oxygen and for systems with a combination of oxygen and nitrogen makes it possible to account for the exceptional role of oxygen. The key structural transformations, determining the formation of the AlN polytypes (the separation of the solid solution into layers with formation of an oxygen-enriched zone, the formation of three-layer oxygen-containing defects as concentration inhomogeneities with an ordered arrangement in such zones) are associated with the development of ascending diffusion. In the case of the 2H AlNO solid solution, the latter may occur only as a result of the stress gradients generated by the aluminium vacancies. The ordered vacancies V_{Al}, disposed in the O–V_{Al} layer, are also 'responsible' for the shear as the final stage of polytype formation.

Thus the polytype formation in AlN is a vacancy-stimulated process, *i.e.* it occurs only in the presence of vacancies in the system. The energy of formation of structural vacancies in AlN is high (according to Cormack,[157] it amounts to 62.998 eV for V_{Al} and 52.108 eV for V_N) and they are therefore manifested in the formation of solid solutions. Among chemical elements the dissolution of which in AlN with formation of vacancies is possible, the nitrogen–oxygen, aluminium–silicon, and nitrogen–carbon pairs satisfy best the isomorphous substitution conditions (isoelectronic structure, chemical indifference, similarity of the atomic radii, and similarity of the electronegativities).

There are few experimental data on the formation of solid solutions in 2H AlN. It has been established[158] that oxygen may substitute up to 1/3 of the nitrogen atoms in thin AlN films; when the degree of substitution is high and T = 800–1000 °C, amorphisation takes place. The AlN in films may be saturated with oxygen up to the compositions AlN_xO_y and γ-Al_2O_3.[141] The dissolution of oxygen in AlN up to 1 at.% induces compression of the lattice,[118] whilst at higher concentrations the lattice is restored (Fig. 7). The fact that the replacement of three nitrogen atoms by oxygen leads to the formation of V_{Al} is generally recognised. A positive energy of mixing is characteristic of the 2H AlNO solid solutions. This is confirmed by the heating thermogram for a highly disperse AlN powder containing ~3 mass% of oxygen.[85] Analysis of the thermogram indicates the presence of endothermic effects on heating up to 1450 °C, which suggest a positive deviation of the solid solution from the ideal state, *i.e.* from Raoult's law.[159] The latter actually determines its separation into layers, *i.e.* a solid-state structural rearrangement with formation of two solid solutions — enriched and depleted in the dissolved element. The segregation of the first solution in the form of a plate bounded by the (0001) surfaces is induced by a heterogeneous mechanism of separation into layers (with participation of basal packing defects).

The solubility of silicon in AlN as an individual element has not been determined. An attempt has been made[160] to investigate this process in AlN films. It was established that, with increase in silicon concentration in AlN, the unit cell parameter a diminishes, whilst c initially increases and then falls. On the basis of these data,

it has been suggested that oxygen is present in AlN films together with silicon.

The dissolution of SiO_2 in AlN has been demonstrated reliably. As in the case of the AlN–O system, this process takes place with formation of V_{Al}:

$$SiO_2 \xrightarrow{AlN} Si_{Al} + 2O_N + V_{Al}.$$

With increase in the SiO_2 concentration in the AlN–SiO_2 system, the parameter c of AlN diminishes (Fig. 13).[161]

Taking into account the literature data,[118, 160, 161] one may assume that the simultaneous dissolution of oxygen and silicon in AlN should be regarded as a result of the mutual influence of the donor (Si) and acceptor (O) impurities. The replacement of aluminium by silicon promotes the appearance of an electron in the system and this should facilitate the dissolution of the acceptor impurity.[162] It is seen from the reaction, presented above, involving the dissolution of SiO_2 in AlN, that V_{Al} is formed on substitution of two nitrogen atoms by oxygen and not on substitution of three atoms as happens on dissolution of oxygen alone. Thus silicon plays the role of the catalyst, in the dissolution of oxygen in AlN.

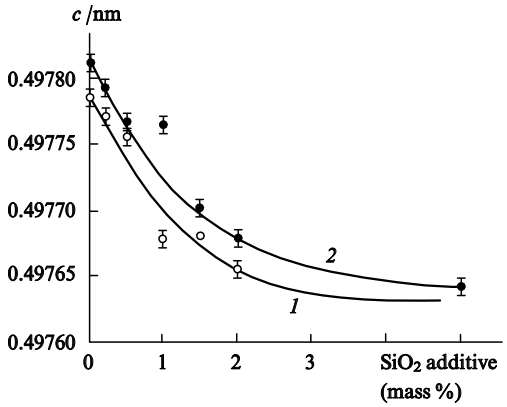


Figure 13. Variation of the parameter c of the AlN unit cell with increase in the concentration of SiO_2 in polycrystalline specimens. Sintering medium: (*1*) air; (*2*) nitrogen.

There is no information about the dissolution of carbon in AlN. Presumably, in conformity with the conditions for isomorphous substitution,[83] carbon substitutes nitrogen in AlN with formation of vacancies in the anionic sublattice (V_N). The structural transformations in the 2H AlN–C solid solution may occur in accordance with the scheme proposed for the 2H AlNO solid solution subject to the difference that their development is controlled by anionic vacancies. Data on polytype formation in the $BeSiN_2$–Be_3N_2 system may serve as confirmation of this hypothesis. In the above system, the vacancies arise in the anionic sublattice of the $BeSiN_2$ wurtzite phase, on the basis of which polytypes actually appear as a result of the periodic segregation of Be_3N_2 layers in the direction of the [0001] axis of the 2H lattice.[163]

On simultaneous dissolution of oxygen and carbon in AlN, polytypes are not formed (for example in the AlN–Al_2OC system).[164] On dissolution, there is in this instance a possibility of the formation of oppositely charged centres, (Al^{3+}–C^{4-}) and (Al^{3+}–O^{2-}), which leads to charge compensation in the AlN lattice without the formation of vacancies. Furthermore, the polarisability of carbon anions is greater than that of oxygen (according to Slabough and Parsons,[165] the polarisability is directly proportional to the ionic volume and the radii of the carbon and oxygen ions are 2.6 and 1.35 Å respectively), *i.e.* carbon shows a greater tendency towards the formation of chemical compounds. This has been confirmed by data on the formation in the Al–N–O–C system of the compound Al_4O_4C with a melting point < 1700 °C, *i.e.* below the temperature at which the 2H AlNO solid solution separates into layers (the necessary stage of the structural rearrangement in polytype formation). It has been established[166] that, in the joint presence of oxygen and carbon in AlN, the phase with the composition $(Al_2OC)\cdot AlN$ may be formed. This composition was regarded[167] as a solid solution of AlN in Al_2OC. In the same study, it was established that, for an AlN content corresponding to 40 mol % of nitrogen, the ordered $Al_{10}O_3C_9N_4$ phase is segregated in the solid solution.

The mechanism of polytype formation in AlN on dissolution of oxygen in the latter, described above, is supported by the following known experimental facts obtained in the study of AlN-based materials.

1. The decrease in the concentration of vacancies when the oxygen content dissolved in AlN is > 1 at.% (*i.e.* in the range of compositions where polytypes can already be formed).[118] The critical nature of this oxygen concentration, which exhibits a radical influence on the AlN structure, has also been confirmed by the analysis of the Raman spectra of the 2H AlN–O solid solution.[168]

2. The fact that the short-period polytypes are incommensurate, which may be attributed to the high concentration of Al_2O_3 layers.[169]

3. The presence of lamellar O-containing segregations in planar AlN defects.[137]

4. The absence of polytype formation in the 2H AlN–O solid solution and the decomposition of polytypes at a high pressure with the appearance of 2H AlN and aluminium oxynitride.[132] This can be explained by the thermodynamics of the development of structural rearrangements at a high pressure: the rearrangements involving the formation of vacancies (as happens necessarily on dissolution of oxygen in AlN) are unfavourable, whilst the rearrangements involving the disappearance of vacancies (which happens on formation of aluminium oxynitride as a result of the dissolution of nitrogen in Al_2O_3) are actually favourable.

5. The agreement between the calculated compositions of the 12H and 15R polytypes in the Si–Al–O–N system and the experimental compositions established by Bando *et al.*[155]

6. The absence of polytype formation in 2H AlN–O in the presence of impurities ensuring the charge compensation of the lattice following the replacement of nitrogen by oxygen (BeO, SiC).[170, 171]

7. The presence of the Al_2O_3 band in the luminescence spectrum of AlN containing up to 2.8% of oxygen.[172]

8. The presence of the Al_2O_3 band in the 51R spectrum of a lamellar AlN crystal made up of multilayer polytypes.[173]

9. The agreement between data on the content of oxygen in the 51R polytype quoted by Youngman and Harris[118] and Oleinik and Shevchenko[142] (6.6 at.% and 8.5 at.% respectively).

6. Beryllium siliconitride and beryllium oxide

Two series of polytypes exist in the Be–Si–O–N system. On the phase diagram, they are located along the line corresponding to the constant cation/anion ratio in the $BeSiN_2$–BeO–Be_3N_2 range of compositions. The available information about these polytypes (based on the data of Shaw and Thomas[163]) is presented in a generalised form in Tables 6 and 7. One series of polytypes are formed on the basis of the 2H BeSiN lattice along the $BeSiN_2$–Be_3N_2 connecting line, whilst another series are formed on the basis of 2H BeO along the BeO–Be_3N_2 connecting line.

The polytypes in the system considered have been observed as individual ternary phases (Be–Si–N and Be–O–N) by Heseby *et al.*[174] in a study of the Si_3N_4–SiO_2–BeO–Be_3N_2 quasi-ternary system along an isothermal section (1700 °C). These phases were identified by X-ray diffraction also in the Si_3N_4–Be_3N_2–BeO system. They were represented as multilayer structures with different M/X ratios and have been described in terms of Ramsdell's symbols.[175, 176] Thompson and Gauchler[176] constructed the Be–Si–O–N phase diagram on the basis of the results of their own studies and those of Heseby *et al.*[174] The regions where

Table 6. The compositions and the parameters c of the unit cell for polytypes of the $BeSiN_2 - Be_3N_2$ series.

Polytype	M/X	No. of layer		Composition		c /Å	
		see [a]	see [b]	I	II [174]	I	II [175]
4H Be_3N_2 [c]	3:2	4	—	Be_3N_2	Be_3N_2	9.693	9.693
9R	4:3	6	3	Be_7SiN_6	—	12.567	—
8H	5:4	4	4	Be_4SiN_4	Be_4SiN_4	19.064	19.22
15R	6:5	6	9	$Be_9Si_3N_{10}$	$Be_9Si_3N_{10}$	35.625	36.32
12H	7:6	4	8	$Be_5Si_2N_6$	$Be_5Si_2N_6$	28.44	29.10
21R	8:7	6	15	$Be_{11}Si_5N_{14}$	$Be_{11}Si_5N_{14}$	49.68	50.98
16H[d]	9:8	4	12	$Be_6Si_3N_8$	—	37.81	—
27R[d]	10:9	6	21	$Be_{13}Si_7N_{18}$	$Be_{13}Si_7N_{18}$	63.74	65.11
$BeSiN_2$ [e]	1:1	—	2	$BeSiN_2$	$BeSiN_2$	4.69	4.69

Note. The following designations have been adopted: I — calculation; II — experiment. [a] The number of Be_3N_2 layer. [b] The number of $BeSiN_2$ layer. [c] The hexagonal phase (a = 2.842, c = 9.706 Å), the distance between the close-packed layers is 2.423 Å. [d] Hypothetical polytype. [e] Orthorhombic ordered wurtzite structure (a = 4.977, b = 5.747, c = 4.674 Å), the distance between the close-packed layers is 2.343 Å.

Table 7. The compositions and the parameters c of the unit cell for polytypes of the $BeO - Be_3N_2$ series.

Polytype	M/X	No. of layer		Composition		c /Å	
		see [a]	see [b]	I	II [174]	I	II [175]
4H Be_3N_2 [c]	3:2	4	—	Be_3N_2	Be_3N_2	9.693	9.693
9R	4:3	6	3	Be_4ON_2	—	21.099	—
8H	5:4	4	4	$Be_5O_2N_2$	—	18.44	—
15R	6:5	6	9	$Be_6O_3N_2$	$Be_6O_3N_2$	34.22	34.58
12H	7:6	4	8	$Be_7O_4N_2$	—	17.19	—
21R	8:7	6	15	$Be_8O_5N_2$	$Be_8O_5N_2$	47.34	47.87
16H[d]	9:8	4	12	$Be_9O_6N_2$	—	35.94	—
27R[d]	10:9	6	21	$Be_{10}O_7N_2$	—	60.47	61.05
BeO [e]	1:1	—	2	BeO	BeO	4.38	4.38

Note. The following designations have been adopted: I — calculation; II — experiment. [a] The number of the Be_3N_2 layer. [b] The number of the Be_2O_2 layer. [c] The distance between the close-packed layers is 2.423 Å. [d] Hypothetical polytype. [e] The distance between the close-packed layers is 2.187 Å.

various polytypes are located were identified on the diagram (Fig. 14).

Clarke *et al.*[177] proposed for the first time a model of the structure of polytypes in the system under consideration. It is based on the motif of a regular defective wurtzite structure with the general formula $M_{m+1}X_m$, where the minimum value of m (m = 2) corresponds to the Be_3N_2 structure. According to the authors,[177] the formation of polytypes is determined by the periodic incorporation of the M_2X layers into the MX blocks of the basic 2H structure of $BeSiN_2$. This model has been confirmed by electron microscope studies on polycrystalline specimens containing the polytypes in the $BeSiN_2 - Be_3N_2$ system: Shaw and Thomas[163, 178] observed regularly arranged planar defects in the structure of the 2H $BeSiN_2$-based polytypes. It was suggested[163] that this structure of the polytypes is due to the formation of defects having a structure and composition different from those of the basic wurtzite structure. Each defect consists of two cubically packed Be_3N_2 layers forming a hexagonal unit cell. These defects promote the transformation of the 2H structure into a set of structures with different phase compositions and volumes of the

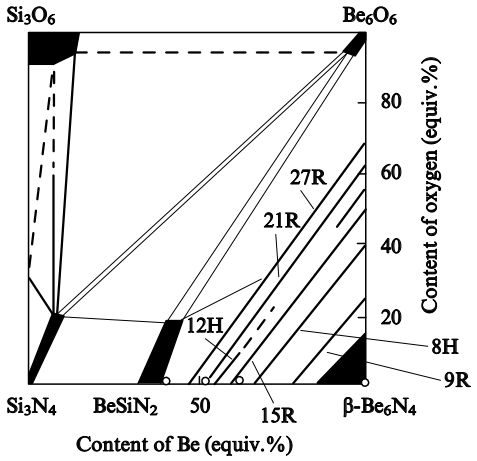


Figure 14. The isothermal section through the Be–Si–O–N phase diagram at 1780 °C.[176]

unit cells. The size of the unit cell is determined by the distance between the defects. According to Shaw and Thomas,[163] the appearance of Be_3N_2 layers is induced by the ordering of the vacancies in the nonmetallic $BeSiN_2$ sublattice and the subsequent exclusion of the resulting sub-layers of vacancies as a result of a crystallographic shift along the (0001) direction. Dislocations with a Burgers vector of the type $1/6\langle 20\bar{2}3\rangle$ were identified in the $BeSiN_2$ structure. The shift probably occurs with the aid of these dislocations.[163] The development of such a shift is responsible for the appearance of the beryllium-enriched planar defects corresponding to the Be_3N_2 composition.

On the basis of the postulates concerning the structure of the polytypes in the $BeSiN_2 - Be_3N_2$ system described above and having adopted a similar model for the structure of the polytypes in the $BeO - Be_3N_2$ system, Shaw and Thomas[163] determined the tentative compositions of a series of polytypes in these systems and calculated the dimensions of the unit cells in the direction of the c axis (Table 7). Evidently these data agree with the experimental results for the polytypes in the Be–O–N system.

7. Boron nitride

As in carbon, polytypes based on three modifications are formed in boron nitride: graphite-like, wurtzite, and sphalerite. The polytypes based on the first modification are formed as intermediate structures in the 2H BN → graphite-like BN transition. This transition, which occurs *via* the mechanism of the explosive martensite transformation, has been observed directly in the study of the 2H BN particles by means of a transmission electron microscope. It involves the type of transformation in which a particle of the initial phase is converted into a particle consisting of the graphite-like BN and the polytypes based on it.[179] On sintering polycrystalline 2H BN specimens, this transformation occurs on the surfaces of the layered region.[180]

The 2H BN → MP + 3C BN transition occurs at high temperatures and pressures. It has been established by electron microscope studies[181] that at P = 5 GPa the transition begins already at 1200 °C and takes place intragranularly *via* a shift mechanism with the aid of Shockley particle dislocations and with a Burgers vector of the type $1/3a[10\bar{1}0]$. As a rule, the transformation results in the formation of a mixture of polytypes. In rare instances, only one polytype is obtained. The 15R polytype has been identified[182] on the basis of 2H BN, whilst in another study[183] the 4H polytype was identified. In the primary recrystallisation stage, which occurs in heterophase crystals (2H BN + 3C BN + MP), the intergranular transformation 2H → 3C, due to the migration of the interface, also occurs on sintering polycrystalline materials at high pressures.[86]

As in the case of the dense cubic phase of carbon (diamond), the 3C BN-based polytypes are formed under the conditions of deformation at high pressures and temperatures. Their formation is associated with micro-twinning (the formation of thin high-density twinned crystals) in 3C BN crystals *via* a single system of planes of the type {111}.[33]

8. Transition metal carbides and nitrides

The formation of multilayer structures is also characteristic of nonstoichiometric Group IV–VI transition metal carbides and nitrides of the type of interstitial phases. Taking into account the crystal geometry and the chemical composition of the interstitial phases (mainly carbides), a series of hypothetical monophase compounds as well as the mechanism of their formation, have been proposed.[184] It was postulated that these phases are formed as a result of the ordered alternation of hexagonal and cubic layers. They were designated in term of Jagodzinski's and Ramsdell's symbols (Table 8).

Many of the postulated phases (including those in the M–N–C system) were identified.[19, 185, 186] The relation between the composition and the number of layers in polytypic structures has been found for certain carbides MC_y (M = V, Nb, and Ta):[184]

y	1	5/6	4/5	3/4	2/3	3/5	1/2

Table 8. The multilayer structures in the interstitial phase type transition metal carbides and nitrides.[184]

Phase	Maximum content of non-metal (at.%)	Types and space groups of the possible types of packing
M_2X	33.3	h(2H); hc(4H); h_3c(8H); h_5c(12H′); h_3chc(6H′)
M_5C_3	37.5	h_3c_2(10H); h_2chc(10H); h_4c(15R); hc_2hc(15R)
M_3X_2	40.0	hc_2(6H); h_2c(9R); h_3c_3(12H); h_2chc_2(12H); h_4c_2(18R); hc_3hc(18R); h_2c_2hc(12H)
M_4X_3	42.8	hc_3(8H); h_2c_2(12R)
M_5X_4	44.4	h_2c_3(5T); hc_4(10H)
M_6C_5	45.5	hc_5(12H); h_2c_4(18R)
MC	50.0	c(3C)

Note. The following designations have been adopted for the space groups: H = $P6_3/mmc$, D_{6h}^4; T — $P\bar{3}m1$, D_{3d}^3; H′ = $P\bar{6}m2$, D_{3h}^1; C = $Fm3m$, O_h^5; R = $R3m$, D_{3d}^5; h and c = layers with hexagonal and cubic types of packing respectively.

Structure	3C(∞)	$(51)_3$	41	$(31)_3$	$(21)_3$	$(32)_3$	2H(11)

Monophase ordered compounds are usually formed in the synthesis in the region of the coupling boundary between monocarbides with a hexagonal close-packed lattice and hemicarbides with a face-centred cubic lattice (this applies also to nitrides)[185, 186] or during the ordering process.[19] In most cases, these compounds are referred to as superstructures. A characteristic feature of the microstructures of many of them, namely the one-dimensional microdomain structure, has been established experimentally: for example, in V_6C_5,[187] Ta_6C_5,[188] Ti_3N_{2-x},[189] and certain vanadium, niobium, and tantalum carbides.[185]

Two models of the ordering in carbides and nitrides of the type of interstitial phases are now known. One of the models takes into account the nonstoichiometry of these substances, namely the presence of vacancies in the nonmetallic lattice. A decisive role in the formation of the ordered state (*i.e.* in the appearance of superstructures) is attributed to the development of the process involving the ordering of the structural vacancies and the N and C atoms in the nonmetallic sublattice.[19] The initial phases are in essence interstitial solid solutions (dissolution of N and C in the M lattice), which implies a redistribution of the nonmetal atoms among the octahedral interstices of the M sublattice. Kolyagin *et al.*[186] explained the formation of the superstructures by the generation of packing defects of various types in the metallic sublattices of the initial hexagonal close-packed and face-centred cubic phases.

The formation of superstructures in superstoichiometric nitrides with deviations from stoichiometry with respect to the metal is attributed to a redistribution of the M atoms and the structural vacancies in the metallic sublattice.[19] It has been suggested that such structures may be formed as a result of the development of various ordering mechanisms. For example, according to the data of Pushchin and Shagaev,[190] the 3C, $6H_2$, 6H, and 4H polytypes were identified by electron microscopy in the Nb–N system on film objects obtained by ionic-plasma sputtering. They are formed in the range of compositions with the ratio M/X close to unity. The 3C polytype is δ-NbN. It is believed[190] that the ordered formation of packing defects in the layers of M atoms of this structure leads to the transition to the 6H and $6H_2$ structures, while the combination of such ordering and the ordering of the vacancies entails the appearance of the 4H polytype (Nb_5N_6 — stoichiometric composition).

The formation of multilayer structures is characteristic also of carbides of the type M_7C_3 (M = Cr, Fe). The formation of polytypes based on the monoclinic and rhombohedral modifications of these carbides is associated with the ordered generation of packing defects and microtwinned crystals.[191] Indeed, the presence of planar defects such as twinned crystals and antiphase boundaries has been established in the above carbides.[192] These defects may be distributed in the basic lattice of the crystals periodically, quasi-periodically, and randomly and depending on this factor, can give rise to modulated, microdomain, and twinned substructures.

9. Oxygen-containing materials

The polytype formation processes in oxygen-containing materials have been little investigated. We shall therefore consider only the main data available in the literature on this problem.

a. Oxides

BeO. Polytypism in BeO has already been discussed. The known and postulated 2H BeO-based polytypes are presented in Table 7.

2H ZnO. There is no information in the literature about polytypism in 2H ZnO. Our studies established that multilayer polytypes may be formed in the grains of polycrystalline ZnO and ZnO with added ZrO_2. The geometrical and morphological characteristics of crystals under the conditions involving the formation of polytypes are similar to the characteristics of AlN. In particular, the polytypes in the ZnO grains arise in lamellar interlayers segregated along the basal plane, as happens in AlN (Fig. 2).

$ZrO_{1/3}$. A series of polytypes are formed in the zirconium oxide $ZrO_{1/3}$, which is obtained on dissolving oxygen in metallic zirconium when the oxygen content varies from 24% to 26%.[193] They are intermediate structures between the rhombohedral (3R) and hexagonal (2H) modifications, 3R has the composition ZrO_x ($x < 1/3$) and 2H has the composition ZrO_y ($y > 1.3$). The 8H, 5H, 12R, and 7H polytypes arise on the basis of 3R, whereas the 10H, 12H, and 14H polytypes are based on 2H. It has been suggested[193] that the formation of multilayer structures is determined by the changes in the packing sequence of the oxygen layers. On dissolution in zirconium, oxygen occupies the octahedral interlayer cavities in the face-centred cubic packing. The ZrO_x structure is characterised by an order in the packing of layers of the type ABC ABC..., whilst ZrO_y is characterised by a packing order of the type AB AB.... With increase in the oxygen concentration in zirconium oxide, the sequence in which the number of layers in the polytypes varies is as follows: 3R → 8H → 5H → 12R → 7H → 10H → 9R → 12H → 14H → 2H.

The formation of a set of incommensurate long-period structures in the ZrO_2-ZrN system in the region with a high ZrO content (the ZrN content was 2.5 mol.% and more) has been established by electron microscope studies.[194] Similar polytypes have been observed in this system also in another study.[195] It has been suggested[194] that the long-period structures are microstructures produced by the intergrowth of the layers of the basic structure (cubic ZrO_2) and the segregations of the rhombohedral oxynitride $Zr_7O_{11}N_2$, *i.e.* they differ in their phase compositions.

There are data on the formation of multilayer structures in titanium, vanadium, niobium,[196] manganese, and silicon[2] oxides. In the last case, they are formed on the basis of a polymorphic modification of tridymite. SiO_2 polytypes such as 2H, 4H, 10H, and 20H have been identified.

Multilayer structures have been observed in the orthorhombic aluminium-enriched mullite. The results of studies by high-resolution electron microscopy led to the conclusion[197] that such structures are formed as a result of the ordering of oxygen vacancies. The latter form cavity channels (giving rise to antiphase boundaries) along the *b* axis, the periodic alternation of which actually promotes the formation of multilayer structures. Computer modelling of the structural transitions in mullite with participation of oxygen vacancies confirmed the proposed model of the formation of such structures. It was concluded that the structure formation processes depend on the excess of aluminium.

Polytypism is characteristic also of β-alumina.[198] Two basic forms of alumina, β′ and β″, having the compositions $NaAl_{11}O_{17}$ and $Na_{5/3}Mg_{2/3}Al_{21/3}O_{17}$ respectively, are considered nowadays as the 2H and 3R structures. The formation of two polytypes based on the β″-form has been observed — 15R and 30R. The polytypes in β″-alumina differ in the number and regularity of the repetition of oxygen layers of two types. In the first, the oxygen is present at the octahedral and tetrahedral sites, whilst in the second it is present at sites with cubic close packing. The layers of the latter type are conducting. On the basis of the structure of the polytypes, Bovin and Keeffe[198] proposed a new way of designating them: they suggested that the figure corresponding to the number of cationic layers between the conducting layers be enclosed in brackets and added to the usual Ramsdell designation, for example 2H(5), 3R(5), 15R(5), and 30R(5). On decrease in the sodium content in β-Al_2O_3, the β‴- and β⁗-structures are formed. The number of cationic layers in the structure of the polytypes then increases. The polytypic forms of β‴-Al_2O_3 are designated correspondingly as 2H(7), while those of β⁗-Al_2O_3 are designated as 3R(7).

The polytypism in $BaMnO_{3-x}$ is associated with change in the oxygen concentration. The change in the polytypic composition of this compound on heating has been investigated in the range 1000–1600 °C as a function of the partial pressure of the oxygen in the surrounding medium ranging from 2×10^{-4} to 2×10^{-1} N m^{-1}.[199] In the range of pressures from 2×10^{-1} to 3×10^{-2} N m^{-2} with x varying from 0 to 0.3, the following polytypes are present in the composition: 15H, 8H, 6H, 10H, and 4H. On increase in x from 0 to 0.3 in the temperature range from 1000 to 1600 °C, the following series of polytypes are formed: 2H → 15H → 15H + 8H → 8H + 15R → 8H → 6H → 10H → 4H. For $x > 0.3$, the 4H structure is formed predominantly.

Two polytypic forms are known for $SrMnO_3$ — α(4H) and β(3C); the perovskite structure is characteristic of the composition $SrMnO_{3-x}$[200] (in contrast to $BaMnO_{3-x}$ the basic structure of which is 2H).[199]

The 4H, 6H, 14H, and 27R polytypes have been identified in barium chromite $BaCrO_3$. A model of the structure of the 6H polytype has been proposed.[201] It is based on the hypothesis of the periodic formation in the basic structure of close-packed BaO_3 layers containing tetravalent chromium atoms in all the octahedral cavities of the oxygen sublattice.

b. Copper-containing metal oxides

Polytypism is characteristic also of layered copper–oxygen compounds belonging to the group of metal oxide superconducting substances. Such compounds are also referred to as cuprates. The available data on polytype formation in substances of this class have been obtained mainly in the study of compounds formed in the following systems: Y–Ba–Cu–O, Bi–Sr(Pb)–Ca–Cu–O, Tl–Ba–Ca–Cu–O, and Hg–Ba–Ca–Cu–O. The polytypes in these substances are regarded as individual phases because they differ in composition. The polytypes are designated by a sequence of figures reflecting the quantitative content of metal atoms in the formula unit, for example $YBa_2Cu_3O_{7-x}$ is designated by 123, YBa_2Cu_5O by 125, and $BiSr_2CaCu_2O_8$ by 1212.

A common feature of the formation of polytypes in superconducting materials is a tendency towards syntaxy, *i.e.* the formation in individual crystals of a mixture of polytypes (Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O,[202,203] Hg–Ba–Ca–Cu–O[204,205]). It has been shown in relation to compounds formed in the Hg–Ba–Ca–Cu–O system that the intergrowth of polytypes in crystals takes place along the same planes, *i.e.* is consistently crystallographically oriented.

The following information is available about the nature of the polytypism in metal oxide superconducting materials. According to Ramesh *et al.*,[206] the formation of polytypes is associated with a change in the composition of perovskite blocks. In polytypes of the Y–Ba–Cu–O system, the composition may vary when additional planes, for example Cu–O, are incorporated into the basic structure. These may also be CuO–YO–CuO layers.[207,208] The results of an electron microscope study of the structure of polytypes have shown[209] that such layers are usually segregated in the vicinity of the Cu–O layers existing in the initial structure. The Cu–O layers are displaced relative to one another by 1/2 of the period *b* of the initial tetragonal structure. The number and relative disposition of the Cu–O planes in polytypes vary. This is responsible for the different contents of the quasi–perovskite blocks (*i.e.* the elementary layers bounded by the Cu–O and $Cu-O_2$ planes) and hence also for the number of layers.[210] The additional Cu–O layers in the phases of the Y–Ba–Cu–O system have been considered[211] as packing defects. The regular introduction of such layers into the 123 structure (after each Cu–O layer present in the initial phase) promotes the formation of the 248 phase.

According to Alekseevskii *et al.*,[212,213] the formation of polytypes in superconducting cuprates is determined by the characteristic features of the coupling of the perovskite blocks as elementary constituents of the structure. Two ways of joining such blocks have been proposed. These lead to the formation of polytypes and superstructures.

The principal characteristics of the commonest polytypes in the Y–Ba–Cu–O system have been surveyed[210] (Table 9). According to the data of Kozo and Wei,[214] the replacement of Y by Ln in this system leads to a new series of polytypes as individual phases: $LnBa_2Cu_3O_{7-x}$ — Ln123, Ln_2BaCuO_5 — Ln211, $LnBa_6Cu_3O$ — Ln163, and $LnBa_4Cu_3O$ — Ln143.

The polytypic transitions in the Y–Ba–Cu–O system may also occur on heating,[215] irradiation by heavy ions,[216] deformation,[217] doping by additives such as Co, Fe, and Al,[218] the replacement of yttrium by the complexes Cu_xC_{1-x}, and partial replacement of Ba by Ca.[219]

There are numerous publications in which questions concerning the ordering of oxygen atoms and oxygen vacancies in compounds of the Y–Ba–Cu–O system are discussed. According to Chushak *et al.*,[220] the ordering of the oxygen atoms takes place in the basal planes. Ising's model has been used to describe this process.[221] On the basis of this model, questions concerning the formation of polytypes in SiC and spinelloids have been discussed.[13–15] The ordering of the vacancies, accompanied by the formation of superstructures, may be not only one-dimensional but also two-and three-dimensional.[222] The formation of superstructures on the basis of the 123 phase has been reported.[223]

Table 9. Characteristics of the polytypes of the homologous series $Y_2Ba_2Cu_{6+n}O_{(14+n)\pm x}$.[210]

n	Formula	Phase (polytype)	No. of CuO planes	K[a]	c /Å	c_0 /Å[b]	T_c /K[c]
0	$YBa_2Cu_3O_{7-x}$	123	1	3	11.763	3.891	91
2	$YBa_2Cu_4O_8$	248 (124)	2	7	27.237	3.891	81.4
1	$Y_2Ba_4Cu_7O_{15-x}$	247	Alternation of one and two planes	13	50.544	3.888	85.5
4	$YBa_2Cu_5O_9$	125	3	4	15.6	3.90	—
6	$YBa_2Cu_6O_{10}$	126	4	9	34.12	3.791	55

[a] The number of elementary layers (quasi-perovskite blocks) in the cell. [b] Thickness of the elementary layer; $c_0 = c/K$. [c] Temperature of the transition to the superconducting state.

The following polytypes are known for the Bi–Sr–Ca–Cu–O system: 2201, 2212, 2223, 2234, and 2302.[224–226] It has been suggested that the formation of polytypes in this system is influenced by Pb, which may substitute Bi,[226] and also by the concentrations of Ca and Cu in the crystallisation medium. It has been shown[225] that the 2201 phase, which crystallises in Bi–Sr–Ca–Cu–O glasses, is segregated only in regions depleted in Ca and Cu. The latter occurs as a result of the formation of compounds of the Ca–Cu–O system. The 2223 phase is also segregated under these conditions. The crystals formed in the system considered consist in most cases of a mixture of polytypes, mainly 2223, 2234, and 2212.[203]

The crystal-chemical characteristics of the phases formed in the Bi–Sr–Ca–Cu–O system have been examined in detail.[224] It was concluded that the 2201 phase is stoichiometric and can be regarded as the basic structure in this system.

The most characteristic phases in the Tl–Ba–Ca–Cu–O system are 2223 and 2212.[227] In the specific synthesis of the 2223 phase by the application of a high pressure, the 2234 phase is also formed.[228] When Ca is replaced by other metals, new phases are formed, for example on its replacement by magnesium a series of phases may be produced — ranging from 12304 to 12034,[229] while the replacement of thallium by copper results in the appearance of the 2201 phase.[230]

The stability of the polytypic structures in Bi- and Tl-containing cuprates were examined as a function of chemical composition[231] within the framework of the Ising model with multispin interaction. The compounds in these systems are represented by the homologous series $A_{2x}B_{2x}Ca_{1-x}CuO_{4x+2}$ (A, B = Bi, Sr or Tl, Ba). It has been shown that, depending on x_0, there may be several equilibrium phases (or ideal polytypes):

Phase	2201	2212	2223	4413	0011
x_0	1	1/2	1/3	2/3	0

For slight deviations of x from x_0, such phases may be regarded as periodic polytypes containing packing defects. For arbitrary values of x, there is a possibility of the combination of a set of disordered phases.

The following main phases have been identified in the Hg–Ba–Ca–Cu–O system: 1212, 1223, 1234, and 1245.[232] They are formed in the synthesis of superconducting phases at both normal[223] and high[233] pressures. On combination of the 1212 and 1223 phases and the 1223 and 1234 phases, crystal-oriented intergrowth takes place.[204] If Hg and Ca are replaced by Pr, *i.e.* in fact on formation of the new system (Hg, Pr)–(Sr, Ca, Pr)–Cu–O, the 1222 phase is formed together with the 1201 and 1212 phases at the normal pressure.[234]

c. Minerals

Polytypism has been observed in a multiplicity of minerals: wollastonite plagioclase, barium feldspar, wenkite, sapphirine;[18,235] kaolinite, chlorite, pyrosmalite, parasite, synchisite, cronstedtite, hydrotalcite, tridymite, coquimbite;[2] mica-like minerals, pyrophyllite;[236,237] ferrite;[238–240] zirconolite;[241] spinel;[2] spinelloids, pyroxenes, and pyroxeenoids;[13,14,242,243] biopyribol;[244] nigerite;[245] phyllosilicates;[246] silicates containing iron layers — berthierine, glauconites, and biotites.[247] (Unfortunately, the available information about the polytypism in minerals is nonsystematic and scattered. Therefore the principal studies in which such information is given are indicated.)

Certain hypotheses concerning the nature of the polytypism in chlorites, micas, and minerals of the kaolinite group, described by Verma and Krishna,[2] are based mainly on the ideas involving different ways of arranging the layers determining the symmetry and the parameters of the unit cells of multilayer structures. It has been postulated that polytypes are formed *via* the displacement of the layers relative to one another for micas, as a consequence of the periodic introduction of structural packing defects along (100) for wollastonite, and as a result of the appearance of antiphase boundaries along (001) for feldspars.

In micas and mica-like minerals (pyrophyllite, talc), the polytypism is due to the different dispositions in neighbouring layers of pairs of cations which are located along a single normal to these layers.[236] The difference is determined by both the number and kind of the cations superimposed in projection on to the plane of the layer. On the basis of these ideas, the authors deduced the polytypic modifications of micas, and also determined to what extent their formation is favoured by energy factors. A smaller number of superimposed cations constitutes a criterion of their being favoured by such factors.

Polytypes such as 84R, 102R, 40H, and 138R have been identified for hexagonal ferrites.[238] Ideas concerning the nature of the polytypism in such ferrites containing Ca, Ba, Pb, Sr, and K have been described.[239,240] It has been suggested that the structure of these ferrites is made up of identical spinel type fragments, the so called S_n layers, which have two orientations. Layers with both identical and different orientations may be coupled in the structure of the ferrites. Connecting structural elements arise on coupling of the layers. In Ca ferrites, such elements are identical for both types of coupling of the layers, whereas in ferrites containing Ba, Pb, Sr, and K they differ in structure and composition. This factor is actually responsible for the fact that a family of polytypes are formed in Ca ferrites and only fragmentary layered structures are produced in the group of Ba and other ferrites.

The following polytypes are known for the $Mg_2Al_4O_8$ spinel: 4H, 5H, 6H, 15H, 15R, and 18R.[2] Horiuchi *et al.*[248] established for the first time that a whole family of new structures — spinelloids — are formed on the basis of this spinel structure. In spinelloids, the packing of the oxygen atoms constituting the framework is approximately cubic; they have the ideal stoichiometry corresponding to the composition AB_2O_4. In their structure, 2/3 of the cations occupy sites with octahedral coordination with the oxygen framework; the remaining 1/3 of the cations have tetrahedral coordination. The cations distributed in the oxygen framework constitute the basic structural unit of spinelloids. In the majority of spinelloids, bands are formed on the basis of the packing of the basic structural units, which is invariant in two orthogonal directions. The variation of the arrangement of these bands in three directions actually determines the formation of the set of spinelloid structures. The polytypes in spinels (mainly in the $NiAl_2O_4$–Ni_2SiO_4 system) have been discussed on the basis of the ANNNI model.[13,14,242] As already mentioned, a satisfactory agreement between the spin model of polytypism and a real system has in fact been obtained in relation to the family of spinelloid structures.

10. Sulfides

A tendency towards polytype formation has nowadays been discovered in the following sulfides: ZnS, CdS,[2] FeS, Fe_3S_4,[12,18] CuS, NbS_2, TaS_2,[12,249] Ti_2S_3,[12] $Ti_{1+x}S_2$,[250] $CrNaS_2$,[12] $ZnIn_2S_4$, $Zn_2In_2S_5$, $Zn_2In_2S_4$, $Zn_3In_2S_6$,[12,251,252] $GaInS_3$,[253] PtS_2, ZrS_2,[151] SnS_2, $Ti_{1.2}S_2$,[249] GaS,[254] and MoS_2.[2,18,249] This phenomenon has been most thoroughly investigated in the first two sulfides and also in titanium sulfide.[249,250,255] For the remaining sulfides, it has only been established without a detailed discussion and analysis of the characteristics of its occurrence. We shall therefore consider the most interesting data for some of the above series of sulfides.

Hitherto 155 polytypic structures have been identified in ZnS obtained under laboratory conditions; in natural ZnS, only 10 forms have been found: the sphalerite phase and five hexagonal and four rhombohedral polytypes.[256]

All kinds of polytypism characteristic of substances with the diamond lattice are manifested in ZnS (Table 1).

On heating, the ZnS polytypes are usually formed as intermediate structures in the wurtzite → sphalerite and sphalerite → wurtzite transitions. The first occurs as a rule during the cooling process after synthesis and the second during heating. An intermediate 4H phase is formed in the first transition;[257] its appearance in combination with polytypes having a large number of layers is characteristic also of the second transition.

Overall, the polytypic composition of ZnS is influenced by soluble impurities (Cu, Al, O). Their concentration may also stabilise a particular polytype. Thus, according to the data of Kukul',[258] the number of layers in the polytypes depends on the Al concentration in the following manner: the 6H polytype is formed mainly for 0.005 mass%, the 4H polytype for 0.04 mass%, and the 2H polytype for 0.1 mass%. With increase in the aluminium and copper content, the concentration of packing defects in ZnS diminishes. It, has been established[259] that the decomposition of the solid solution of Cu and O in ZnS promotes the stabilisation of the 3C phase.

The transitions of the hexagonal ZnS polytypes to the 3C phase occur under various load conditions without, special heating: on grinding in a mortar,[260] on grinding-polishing,[261,262] on oriented (to develop the basal slip) uniaxial loading,[263] and on dynamic compression.[264] According to Abdikamalov *et al.*,[263] the conversion of the metastable hexagonal polytypes into the sphalerite phase occurs as a result of plastic displacements in the (0001) plane with the aid of partial Shockley dislocations. It is believed[265] that the transition is achieved *via* a layer-by-layer reorientation and may be referred to as deformation recrystallisation.

According to the generally accepted view, the polytypism in ZnS is due to the regular breakdown of the packing of the basal layers as a result of the ordered introduction of packing defects along the (111) and (0001) planes for the 3C and 2H phases respectively. Overall, in the majority of cases the mechanisms of the formation of polytypes in ZnS have been considered not individually but in combination with SiC as a structural analogue. The known theories of the formation of polytypes, briefly considered above in connection with the analysis of the polytypism in SiC, are equally attributed by their authors also to ZnS.

Multilayer polytypes are also characteristic of the compounds $Zn_2In_2S_4$, $Zn_3In_2S_6$, and $Zn_2In_2S_5$, which are formed in the $ZnS-In_2S_3$ system.[251,252] The following structural characteristics have been discovered for such polytypes: the disposition of the indium atoms in the octahedral and tetrahedral cavities and of zinc atoms only in tetrahedral cavities; the presence of layers and packets of cationic vacancies; a marked distortion of the ideal spherical packing of the sulfur atoms. According to the data of Donina *et al.*,[251] polytypes with the same composition and with identical and different parameters c are manifested for the compound $Zn_2In_2S_4$). A different motif in the alternation of sulfur atoms is characteristic of polytypes of the latter kind.

Polytypes are also formed in the $GaInS_3$ system.[253,266] They have the composition $(A,B)_{n-x}S_{n+1}$ ($n > 3$) and are characterised by the fact that the n-stacked layers, consisting of octahedral and tetrahedral networks, are distributed among close-packed sulfur atoms.

The iron sulfide polytypes have been most thoroughly investigated in relation to pyrrhotites of natural origin (overall formula $Fe_{1-x}S$) obtained from different deposits.[18] The polytypes of this substance usually differ in the number of iron and sulfur atoms and are considered in most cases as individual stoichiometric phases. For example, the 4C and 2C polytypes have the compositions Fe_9S_{10} and $Fe_{11}S_{12}$ respectively. However, there are also polytypes with a wide region of homogeneity, *i.e.* having a nonstoichiometric composition. It has been suggested that the formation of polytypic structures and iron sulfides is associated with the ordering of the metal vacancies in the structure.

The most detailed data about polytypism in the Ti–S system have been published by Palosz[249] and Trone and Huber.[255] The formation of polytypes with different numbers of layers in the system depends on the temperature.[255] The 12R, 12H, 48R, and 696R polytypes are segregated at 800 °C and the 4H, 2H, 8H, 24H, and 40H polytypes are segregated at 900 °C. The polytypes differ in composition: TiS_2 for 2H, $Ti_{2+x}S_4$ for 4H, and Ti_8S_{12} for 12R. It has been suggested that the formation of polytypes is associated with the variation of the concentrations of Ti and S atoms in the layers. On this basis, schemes have been proposed for the arrangement of the atoms in the direction of the basal axis for certain polytypes.[255]

In the compound $Ti_{1+x}S_2$, ten polytypes with hexagonal and rhombohedral symmetries were identified.[250] The presence of screw dislocations in the basal plane has been observed in $Ti_{1.18}S_2$ crystals by X-ray topography, which may serve as confirmation of the decisive role of these defects in the formation of polytypes.

Data concerning the possibility of the formation of polytypes in MoS_2 and GaS have been published.[2,249,254] The polytypes in MoS_2 may be formed as a result of the alternation of layers with hexagonal and rhombohedral types of packing.[2]

11. Halides

Among halides tending to form polytypes, one may identify CdI_2, $CdBr_2$, PbI_2, and AgI; the phenomenon of polytypism has been most thoroughly investigated in these substances.[2,249] Polytypes have been observed also in the following halides:[151] Mg, Mn, Fe, and Co dibromides and Ti, V, Mn, Fe, Zn, and Co diiodides.

Cadmium and lead dihalides are isostructural. Octahedral coordination of the metal ions is characteristic of these compounds. The 4H, 2H, and 6R (especially 4H) polytypes are most common. Other polytypes have been specified.[2,249,267] The largest number of polytypes (109) have been found for CdI_2.[268] It has been suggested that the polytypism in the halides considered is associated with the ordered introduction of structural packing defects.

The following series of polytypes have been identified in AgI: 2H, 4H, 8H, 12H, and 16H.[269] The absence of multilayer structures with rhombohedral symmetry as well as the widest occurrence of the 4H polytype should be included among the characteristic features of the formation of polytypes in this substance.[2]

12. Selenides and tellurides

Polytypism is characteristic of the following substances in the group of selenides: InSe,[12,254] GaSe,[254,270] CdSe,[271] ZnSe,[272] $SnSe_2$,[249] $TaSe_2$, $NbSe_2$, Bi_2Se_3, In_2Se_3, and $Pb_2Bi_2Se_5$.[12] Few data are available on the formation of polytypes in these substances. The 24H polytype has been identified by X-ray diffraction in the CdSe crystals obtained from the gas phase.[271] According to the data of Ollitrault-fichet *et al.*,[270] the following series of polytypes have been observed in GaSe: 4H, 9R, 12R, and 15R. The 2H, 4H, and 3R polytypes are known for TaSe while the 2H,[210] and 4H (see Ref. 2) polytypes are known for $NbSe_2$.

Polytypes are also known in the group of tellurides: CdTe, ZnTe,[273] In_3Te_4, Sc_2Te_3, and Ge_2Te_3.[12] The 15R and 2H poly-

types have been identified in ZnTe crystals grown from the gas phase; the 12H polytype, contained in the 3C phase, has been found in CdTe crystals obtained under analogous conditions.

Among the gallium compounds, polytypism has been observed in GaSe,[254] GaP,[274] and GaAs.[275] The 6H polytype has been identified in the last compound.

III. Practical aspects of polytypism

The influence of polytypism on the properties of nonmetallic crystalline materials has been little studied. We shall consider this problem in relation to several materials.

Various SiC polytypes (mainly 3C, 6H, 4H, 15R, 8H, and 10H) are distinguished by the following properties: the width of the forbidden band; the width of the exciton forbidden band; the effective mass of free electrons; the Hall mobility of electrons; electrical conductivity; luminescence; the energy of phonons; ionisation energy; relative permittivity; the minimum in the conductivity band both as regards position and energy.[2, 6, 38, 39, 276–279] Other properties of the polytypes also differ.[280, 281]

The differences in the electrophysical properties of the SiC polytypes make it possible to regard them as a family of wide-band semiconducting materials; However, owing to the difficulty of growing crystals and films with a specified polytypic composition, only the 6H polytype of silicon carbide is used nowadays as a semiconducting material.[279]

By regulating the polytypic transitions in SiC (3C → 6H, 3C → 4H, 6H → 4H), it is possible to control the subgranular and granular structures in polycrystalline materials. Such transitions promote the formation of a one-dimensional microplastic substructure in the grains, the development of anomalous recrystallisation leading to the formation of self-reinforced materials, and the occurrence of collective recrystallisation of the 'grain to grain type'. Questions concerning the formation of self-reinforced SiC materials of different types have been examined.[87, 282] It has been shown that the addition of boron, aluminium, and their compounds, which activate the 3C → 4H and 6H → 4H transit ions, is effective for the preparation of such materials. The self-reinforced SiC materials are very strong and are distinguished by chemical and structural stability at elevated temperature (> 1300 °C). The latter is determined by the presence of reinforcing grains in the form of plates bounded by basal surfaces; the shape factor for such grains may amount to 10–20. It follows from the data quoted by the present author[87] that the bending strength of the self-reinforced materials may reach 1000 MPa and may change insignificantly with increase in temperature up to 1500 °C.

The formation of polytypes in aluminium nitride has the opposite effect on properties such as thermal conductivity and strength. With increase in the number of multilayer polytypes in the AlN + Al_2O_3 and AlN + SiO_2 the polycrystalline materials, the thermal conductivity diminishes.[283, 284] This is induced mainly by the increase in the length of the interfaces between different structural states in the material as a result of the segregation of polytype interlayers within the grains or of grains consisting of multilayer polytypes. The formation of polytypes in AlN, like that in SiC, promotes the formation of self-reinforced materials. The mechanism of the formation of such materials has been examined in detail.[85] It is possible to obtain three types of microstructure of the self-reinforced AlN. Such microstructures may be made up, firstly, of grains reinforced by interlayers, comprising polytypes in the form of plates. Secondly, they can be produced by the combination of grains with interlayers and fragments of individual grains in a lamellar form; thirdly, they can consist predominantly of lamellar grains. The microstructure of the second type is the most characteristic (Fig. 15). Our studies established that three types of grains and six varieties of interfaces can be distinguished in a material with such microstructure.[285] The nature of the differences between the grains is fully determined by the presence of the AlN polytypes in the material. All the varieties of grains and interfaces are noted in the scheme in Fig. 15 and their most typical combinations and morphological characteristics are also shown.

The formation of self-reinforced AlN materials, due to deformation of polytypes as in the case of SiC, is a positive factor. Such materials are distinguished by improved strength properties at both normal and elevated temperatures. Data indicating the strengthening of the AlN materials obtained under the conditions of polytype formation with oxygen-containing additives such as TiO_2, $MoSi_2$, TiC, and TiN (in the last three compounds, the oxygen is present as an impurity) have been published.[286] The results presented by the present author[87] indicate that self-reinforced AlN materials retain their strength up to 1500–1600 °C. Consequently such materials may be used also at high temperatures.

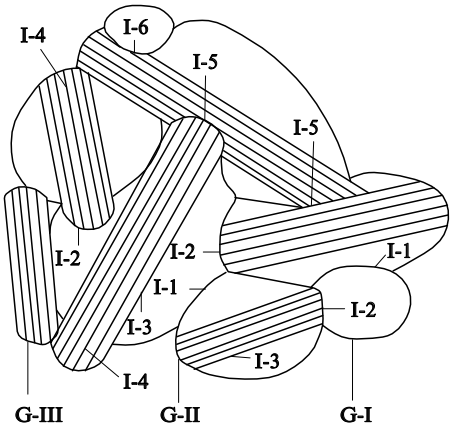


Figure 15. Schematic illustration of the microstructure of a self-reinforced AlN material characterised by the presence of three types of grains and six varieties of internal interfaces. Grain composition: G-I — 2H AlN–O solid solution; G-II — 2H–AlN matrix combined with a plate made up of MP; G-III — individual MP grains; I-1, I-2, I-5, I-6 — intergranular interfaces; I-3, I-4 — intragranular interfaces.

On the basis of the ideas concerning the formation of polytypes in AlN developed by Oleinik and Shevchenko[142] and the analysis of a large number of literature data on this process in AlN materials, it is possible to formulate the physicochemical principles governing the selection of additives to AlN in order to obtain constructional and heat conducting materials. These principles take into account two evident factors. Firstly, in virtually all AlN powders obtained by different methods there is bound oxygen on the surface (aluminium oxides, hydroxides, or oxynitride).[287] Secondly, the formation of polytypes as a necessary stage in the structural preparation for the production of a self-reinforced material occurs under conditions involving the formation of the 2H AlNO solid solution, which is stable up to 1700 °C and is formed with the appearance of vacancies in the aluminium sublattice.

Since the vacancies promote a decrease in the thermal conductivity of AlN,[288] it is necessary to refine AlN with respect to oxygen or to neutralise the vacancies in order to obtain materials for heat-conducting purposes. The preparation of materials involving the formation of AlN polytypes requires the use as additives of either oxides which do not form stable compounds with Al_2O_3 up to 1700 °C and the dissolution of the cations of which in AlN does not promote charge compensation in the lattice on substitution of nitrogen by oxygen or nonoxide compounds (these are a source of oxygen as an accompanying impurity) which do not form stable compounds with oxygen upto 1700 °C and the dissolution of which in AlN does not promote charge compensation in the lattice on substitution of nitrogen by oxygen.

The following approaches have to be used in order to create materials for heat-conducting purposes.

Firstly, it is necessary to use as additives oxides which form stable compounds with Al_2O_3 up to 1700 °C and their stability is higher than that of the 2H AlNO solid solution at $T > 1700$ °C (Y_2O_3 and CaO are the most effective) and oxides which do not interact with Al_2O_3 and the joint dissolution of the cations and anions of which ensures the charge compensation of the AlN lattice (a typical example of such an additive is BeO).

Secondly, it is necessary to sinter the materials at high pressures and temperatures. Since the formation of vacancies is difficult at high pressures, the 2H AlNO solid solution is not formed. The oxygen contained in the initial AlN powder is bound as Al_2O_3, which is segregated as disperse particles along the grain boundaries in the sintered material.[132] Data concerning the formation of a AlN material with a thermal conductivity up to 185 W m^{-1} K^{-1} [289] constitute convincing confirmation of this. Our investigations established [290] that preliminary treatment of the initial powder in shock waves promotes the refining of AlN on subsequent sintering *via* the formation of oxygen-containing disperse segregations in the grain boundaries.

The polytypes of copper-containing metal oxide compounds (cuprates) are distinguished by the temperature of the transition to the superconducting state (T_c). This is caused by their different contents of conducting copper-containing layers. As an example, one may point to data on T_c obtained [291] for certain polytypes of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ homologous series (n is the number of CuO_2 layers). The 2201 ($n = 1$), 2212 ($n = 2$), and 2223 ($n = 3$) phases have $T_c = 7, 80$, and 110 K respectively. It has been shown by means of model calculations that T in phases with $n > 4$ may reach 142 K.

The relation between c_0 and T_c has been discovered (Table 9).[210]

Another group of substances which tend to form polytypes and in which this phenomenon has a useful application are the carbides and nitrides of the type of interstitial phases. The conversion of the structure of these phases into a microdomain form, associated with the formation of multilayer structures, is known to strengthen the phases. The degree of strengthening is then determined by the size (the thickness of the cross-section) of the domains, which may be regulated by altering the rate of cooling.[292]

IV. Conclusion

The data described permit several general and specific (referring to particular groups of substances) conclusions about the formation of polytypes in nonmetallic materials.

Polytypes are formed both at normal and high temperatures and pressures. Their formation reaction occurs in substances in the form of powders, films (single-crystal and polycrystalline), isolated single crystals, and compact polycrystalline materials; the reaction is characteristic of substances with different energies of the packing defect (from 5.4 ± 1.8 mJ m^{-2} for ZnS to 279 ± 41 mJ m^{-2} for diamond),[293] different types of crystal lattice, and different types of chemical bonds; it can occur both during the growth of the crystals and films and on treatments of different kinds (heating, doping, deformation, irradiation, *etc.*).

Polytypic transitions may be of two kinds depending on the nature of their development: intracrystallite and intercrystallite. The intragranular formation of polytypes is associated with the periodic formation of planar defects of different types in the basic structure.

For example, such defects in SiC, ZnS, CdS, CdI_2, $CdBr_2$, PbI_2, Si, C (graphite, 2H), BN (graphite-like), and wollastonite are structural packing defects; for B_4C, BN (3C), C (3C), and M_7C_3 (M = Fe, Cr), these are microtwinned crystals; for mullite and barium feldspar, these are antiphase boundaries; for FeS and $Zn_3In_2S_6$, they are layers of ordered vacancies; for Group IV – VI transition metal carbides and MoS_2, they are layers with face-centred cubic or hexagonal close packing; for BeO, $BeSiN_2$, ZrO_2, AlN, and $YBa_2Cu_3O_{7-x}$, they are layers of other phases. Defects consisting of layers differing from the basic structure by the elemental composition and packing of atoms (β-Al_2O_3), the disposition of cations in adjoining layers (micas, talc), the motif in the alternation of like layers ($Zn_2In_2S_4$), the number of constituent like atoms (compounds in the Ti – S system), the coordination number of like atoms ($BaCrO_3$), and the arrangement of basic structural units (spinelloids, zirconolite) are characteristic of certain ceramics; planar defects in the arrangement of chains of SiO_2 tetrahedra are typical for hexagonal ferrites and biopyribol.

The presence of defects such as the elements of the structures of polytypes in many substances (for example, SiC, AlN, $BeSiN_2$, and BN) has been confirmed experimentally and in many instances their formation has been postulated on the basis of crystal-chemical and substructural characteristics of substances. Intergranular polytypic transitions have now been discovered only for substances with diamond-like lattices (SiC, AlN, BN). They are due to diffusion and occur in the following cases: (a) on migration of the boundary between grains made up of different polytypes (SiC, AlN — Fig. 3); the development of such transitions is always preceded by intragranular crystal-oriented phase and (or) polytypic transformations;[86] (b) under the conditions of recrystallisation *via* a liquid phase (deposition of 6H SiC layers on a 6H SiC support on recrystallisation of the 3C phase *via* eutectic melts of metals);[294] (c) on recrystallisation *via* the gas phase (sublimation growth of crystals and films).[279]

In many substances, the polytypes differ in composition, *i.e.* they actually constitute a set of stoichiometric phases. The most typical representatives of such substances are AlN, BeO, $BeSiN_2$, ZrO_2, superconducting ceramics, and compounds in the Ti – S, Fe – S, *etc.* systems.

In the group of diamond-like phases, the energy of the packing defects exerts an appreciable influence on the type of planar defects in the basic lattice, *i.e.* on the block coupling boundaries consisting of layers with identical packing of the atoms.

In the case of low energy of the structural packing defects, the formation of polytypes is determined by this type of planar defects regardless of the formation conditions. SiC and ZnS, in which all kinds of polytypism occur (growth, deformation, and concentration polytypism), may serve as a typical example.

In substances with a diamond-like structure, a high fraction of ionic bonding, and a high packing defect energy (AlN, BeO, $BeSiN_2$), a special type of concentration polytypism occurs as a result of the regular segregation of two-dimensional layers of the second phase in the basic layers of the 2H structure. Different polytypes in substances of this group may be represented by a consecutive series of ordered stoichiometric phases corresponding to a definite ratio M/X.

The formation of multilayer polytypes based on cubic phases on carbon and BN at high temperatures and pressures indicates the possibility of the transition of these phases to dense hexagonal ones, *i.e.* lonsdaleite and 2H BN respectively. This can be accounted for as follows: In polytype formation processes in diamond and 3C BN in the region of their thermodynamic stability, a decisive influence on the development of this process is exerted not by the chemical driving force (it is the driving force of the phase transition) but by the stresses arising under the influence of an external load. The latter is due to the fact that the geometry of the plastic displacements, inevitably arising on deformation in the cubic phases of diamond and BN, coincides with the slip geometry inducing the deformation rearrangements of these phases to dense hexagonal phases.

The formation of polytypes during growth and the polytypic transitions on treatment (heating, doping, deformation) in the bulk of nonmetallic crystals are processes involving a relaxation structural rearrangement, which takes place *via* the regular formation of planar defects of different nature in the crystal lattice. Such defects are produced mainly in only one crystallo-

graphic direction. This is responsible for the regular modulation of the lattice parameter of the basic structure and for the formation of a new structure from it and modulating defects. The nature of the planar defects is determined by the crystal geometry of the lattice of the substance, which determines the energetically favourable structural relaxation mechanism. The minimum lattice energy increment following the introduction of defects is determined by three factors: the nature of the defects, the mechanism of their coupling with the basic (matrix) structure, and the nature of the distribution of defects determining the minimisation energy of their interaction (elastic, electronic, phonon, *etc*.).

Intercrystallite polytypic transitions may occur for diamond-like phases (SiC, AlN, BN). Their development is determined by the orienting effect of the force field of the crystal-support lattice. In this case, we have only the inheritance of the packing order of the atoms of the polytype-support in the layer formed on the support as a result of the recrystallisation of another polytype *via* the solid, liquid, and gas phases.

It appears that at the present time there are grounds for classifying polytypism as the fourth kind of fundamental structural rearrangement (together with the three classical kinds — plastic deformation, polymorphic transformation, and recrystallisation). Like the known types of rearrangements indicated above, polytypes may be formed not *via* one but *via* several structural mechanisms of the transformations.

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