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Incommensurate suprastructures: new problems of inorganic solid-state chemistry

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Abstract. Data on a new class of inorganic incommensurate intergrowth suprastructures, *viz*., layered misfit compounds, are surveyed and systematised. Physical properties of misfit suprastructures are discussed. Possible mechanisms of the effects of the electronic structure and incommensurability on the structural elements of suprastructures and on their recognition in molecular ensembles are considered. The general criteria for self-organisation of incommensurate suprastructures are proposed and conditions for the fragmentation of one of the sublattices (*i.e*., conditions for the formation of nanocomposites) are given. The bibliography includes 82 references.

I. Introduction

The term 'supramolecular chemistry' was introduced by the Nobel laureate J-M Lehn in 1978. He defined this field as the chemistry beyond the molecule, which describes complex aggregates formed as a result of association of two (or more) chemical species linked by intermolecular forces.[1] In succeeding years, this new interdisciplinary science whose language, definitions and concepts are still in their developmental stage has been progressing rapidly.[2]

It should be noted that the range of subjects studied in supramolecular chemistry is being steadily extended, which generates a need for the discussion of some limitations on their choice, in particular, restrictions imposed by the requirements of the geometric and topological correspondence of structural elements upon self-organisation of supramolecular ensembles. As shown below, these limitations are of fundamental importance particularly in the case of inorganic suprastructures because their structures are substantially affected by the rigidity of conjugated extended structural elements. Thus it was demonstrated[3] that a guest – host system, which governs differences in the principles of construction of supramolecules based on the structural organisation of the host (three-, two-, one- or zero-dimensional structures), is better suited to the classification of inorganic subjects of supramolecular chemistry.

Incommensurability between a guest and a host is rather frequently observed in inorganic guest – host systems, which can lead to structural and morphological changes in the supramolecular ensemble as a whole. The problem of incommensurability has been stated and considered in most detail within the framework of supramolecular chemistry dealing with incommensurate intergrowth structures. Studies in this field were started more than a decade ago.[4] Among these structures are inorganic compounds with crystal lattices consisting of two (or more) sublattices whose periods are noticeably different (at least in one direction). The term 'misfit' is finding increasing use for the description of such compounds.

Two types of compounds with incommensurate structural elements, *viz*., linear (one-dimensional) and layered (two-dimensional) structures, are known.[5] Systems characterised by a one-dimensional (chain) structure of the guest sublattice (substructure) belong to the linear type (these structures are also said to be columnar misfit structures). Generally, the sizes of the 'columns' correspond to the size of the host matrix in the *ab* plane perpendicular to the axis of the column, whereas the incommensurability is associated with its *c* axis. These structures are exepmlified in crystals of $Hg_{3-x}AsF_6$ containing $-Hg-Hg-$ chains, which are located in cavities formed by AsF_6 octahedra,[4] and in compounds of the $A_{1-x}Cr_2X_{4-x}$ series (A = Ba, Sr, Eu or Pb; X = S or Se; $x = 0.29$).[6] The structure of one compound of this series, *viz*., $Eu_{1-x}Cr_2Se_{4-x}$, is shown in Fig. 1. This compound is of interest because it contains two types of one-dimen-

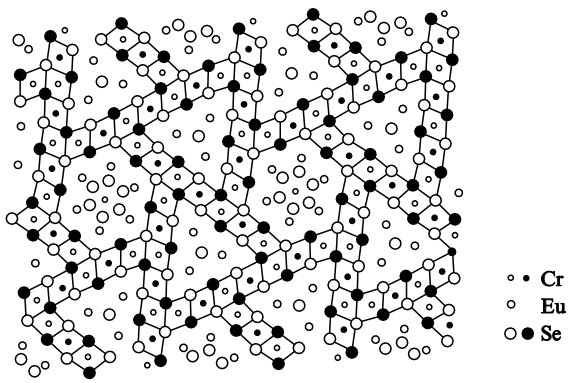


Figure 1. Structure of $Eu_{1-x}Cr_2Se_{4-x}$ (projection along the incommensurate axis).[5]

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sional guest sublattices, *viz*., $Eu_6Cr_2Se_6$ and Eu_3Se, which thread the framework of the host $Cr_{21}Se_{36}$.

Suprastructures with incommensurate layers belong to layered misfit structures. In these structures, as in columnar misfit substances, the incommensurability is manifested only in one crystallographic direction along which the layers are aligned. These subjects are not new, since different combinations of crystallographically incommensurate layers (for example, gallium adsorbate on the surface of single-crystal silicon [7] and some other epitaxial systems) have long been known and have been well characterised. Among layered misfit structures, synthetic complex chalcogenides of the general formula $(MX)_{1+x}(TX_2)_m$ (M = Sn, Pb, Bi, Sb or Ln; T = Ti, V, Nb, Ta or Cr; X = S or Se; $x = 0.08-0.28$; $m = 1, 2, 3...$) have been studied in most detail. These compounds represent analogues of the well-known minerals, *viz*., cylindrite $[(Pb,Sb)S]_{1.38}(Sn,Fe)S_2$,[8] franckeite $Pb_5FeSn_3Sb_2S_{14}$ (see Ref. 9) and some other minerals.[10]

The rather high thermodynamic stability of inorganic incommensurate compounds calls for revision of the existing concepts of the topological 'laws' of construction of supramolecular structures. When constructing incommensurate structures, researchers face two problems. The first problem is associated with the limiting values of the incommensurability up to which the structural elements (substructures) retain their capacity for self-organisation. The second problem is related to the consequences of this self-organisation. In the course of self-organisation of the suprastructure, forces responsible for the retention of the rigidity of its constituent substructures compete with forces linking these substructures to form a single suprastructure. This competition leads to various structural and morphological changes in the ensembles formed.

Since the discovery of incommensurate intergrowth structures, no structures possessing the incommensurability in more than one crystallographic directions have been found, *i.e*., the topological principles of the construction of these compounds are rejected only partially. Nevertheless, even 'one-dimensional' incommensurability gives rise to very interesting properties of inorganic crystal structures.

On the whole, problems associated with the structures, phase stabilities and properties of incommensurate intergrowth suprastructures have not been adequately investigated, though, in our opinion, these problems are of importance for both inorganic supramolecular and solid-state chemistry.

In particular, one of the fruitful lines of investigation of incommensurate structures may be associated with an apparent analogy of the mechanisms of formation of intercalates A_aTX_2 (A is a donor species and TX_2 is a layered dichalcogenide matrix) to those of layered misfit compounds (with the same matrices).

It is also worthy of note that studies dealing with layered misfit compounds have been aimed mainly at searching for new combinations of incommensurate substructures, developing procedures for their structural identification and studying their physical properties. We believe that studies of layered misfit structures are of interest not only because of unusual properties of these compounds, but primarily because of considerable prospects of their application due to evident possibility of the preparation of materials possessing unique electrophysical and magnetic characteristics (if only due to the nontrivial behaviour of conduction electrons in incommensurate crystal fields).

II. Synthesis and structures of misfit compounds

Several procedures for the synthesis of incommensurate suprastructures are known. The majority of layered misfit structures $(MX)_{1+x}(TX_2)_m$ have been prepared by solid-phase high-temperature synthesis starting from the elements or the corresponding binary compounds (MX and TX_2). Generally, suprastructures with M = Sn, Pb, Bi or Sb are formed at about 800–900 °C,[11–16] whereas suprastructures with M = Ln are formed at 1050–1350 °C.[17–20] In all cases, the syntheses are completed in several days.

In a number of studies, layered misfit structures were prepared by slow heating of the starting mixtures to temperatures at which the synthesis started. Then the mixtures were kept at this temperature for several days and the resulting specimens were slowly cooled. Procedures for the synthesis of layered misfit compounds involving quenching of specimens from high temperatures (see, for example, Refs 12 and 16) were also reported. Unfortunately, the dependence of the properties of the resulting specimens on the mode of cooling was not examined.

Most of the known misfit compounds were prepared using stoichiometric amounts of chalcogenides MX and TX_2 $(1:m)$ based on the formula $(MX)(TX_2)_m$ (*i.e*., at $x = 0$), although the compositions of the resulting substances are described by the formula $(MX)_{1+x}(TX_2)_m$, where x is distinct from zero. Generally, syntheses of misfit compounds from the elements were carried out using a small excess of the corresponding chalcogen to accelerate the reaction (see, for example, Ref. 15).

A procedure for the preparation of layered misfit suprastructures (especially, based on REE) from the corresponding ternary oxides by their heating in a graphite boat under a stream of a mixture of hydrogen sulfide and an inert gas at 1300–1350 °C was also described.[5] In particular, this procedure was used for the preparation of $(LaS)_{1.19}CrS_2$.

Single-crystalline specimens can be synthesised by the transport reaction method. Traditionally, iodine [19,20] or chlorine [14] serves as the transporting agent. (It was mentioned that crystals were formed in the cooling zone of a furnace.) Crystals of '$PbNbS_3$' and '$LaNbS_3$' were grown with the use of an admixture of $(NH_4)_2PbCl_6$, which decomposed at high temperature to form $PbCl_2$, NH_4Cl and Cl_2.[17] Apparently, the chlorine liberated acted as the transporting agent.

As mentioned above, layered misfit suprastructures of the $(MX)_{1+x}(TX_2)_m$ type consist of layers of two substructures, *viz*., MX (guest) and TX_2 (host). The guest layer (Q layer) has a pseudocubic NaCl-type lattice and the host layer (H layer) represents a 'sandwich' of hexagonal networks built up from X atoms. Atoms of the transition metal T are either in trigonal-prismatic (Nb or Ta) or octahedral (Ti, V or Cr) environment formed by X atoms (Figs 2 and 3).[21–24] Thus the trigonal-prismatic and octahedral environments about the T atoms are observed in the structures $(SnS)_{1.17}NbS_2$ (see Ref. 24) and $(PbS)_{1.18}TiS_2$,[21] respectively.

Layered misfit compounds differ in the number of the host layers per guest layer (for example, 1Q/1H, 1Q/2H or 1Q/3H).[5] Therefore, these compounds are described by the general formula $(MX)_{1+x}(TX_2)_m$, where the index m is the number of TX_2 layers per unit cell of the suprastructure along the c axis. Mono- ($m = 1$) and bilayer ($m = 2$) structures (Fig. 4) prevail. The arrangement of the structural elements along the b axis can also be different due to the presence of two extreme stacking sequences for the substructures. In the case of a body-centred (CC) arrangement of MX and TX_2 substructures, their c axes coincide, whereas in the case of a face-centred (FF) arrangement, these axes are shifted

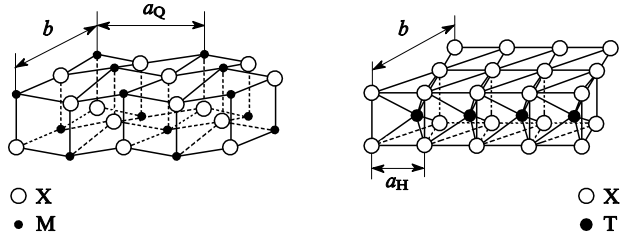


Figure 2. Substructures MX (Q layer) and TX_2 (H layer) with incommensurate lattice parameters (a_Q and a_H).

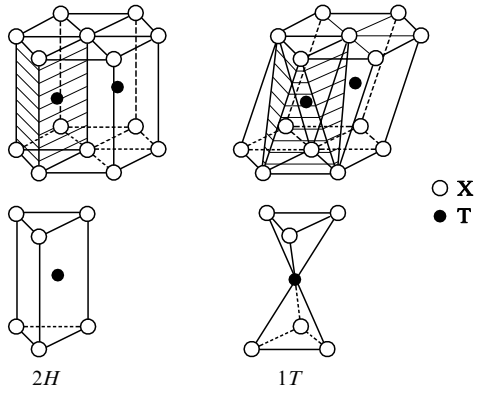


Figure 3. Coordination of the T atoms in the trigonal-prismatic (2*H*) and octahedral (1*T*) polytypes of the TX_2 substructure.

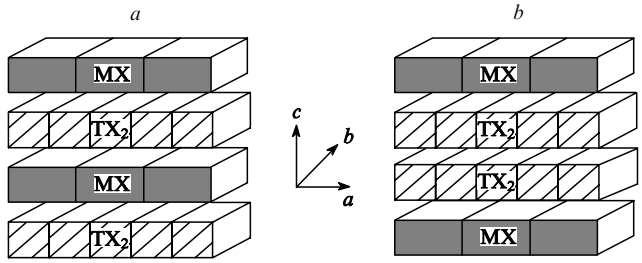


Figure 4. Schematic representation of monolayer (*a*) and bilayer (*b*) misfit structures.

relative to each other by $a/2$. Intermediate modes (CF and FC) of arrangement of MX and TX_2 units were also found (Fig. 5).[5]

The limiting stoichiometry of the suprastructure $(MX)_{1+x}(TX_2)_m$ as a whole is determined by the ratio between the parameters a of the host and the guest ($a_H : a_Q$), which can change from 0.64 [for $(YS)_{1.28}CrS_2)$][22] to 0.54 [for $(BiS)_{1.08}TaS_2$].[23] Here, $x = (4/2)(a_H/a_Q) - 1$ (4/2 is the ratio between the numbers of the MX and TX_2 formula units in the unit cell of the suprastructure). The parameters a_H and a_Q of the unit cells of selected layered misfit compounds are given in Table 1.

The application of the X-ray powder method and X-ray structural analysis to studies of misfit structures presents problems because the symmetry of these compounds should be described by four-dimensional space groups.[4,17] It was also demonstrated that the precise identification of misfit structures is complicated by the following interrelating facts: by the presence of

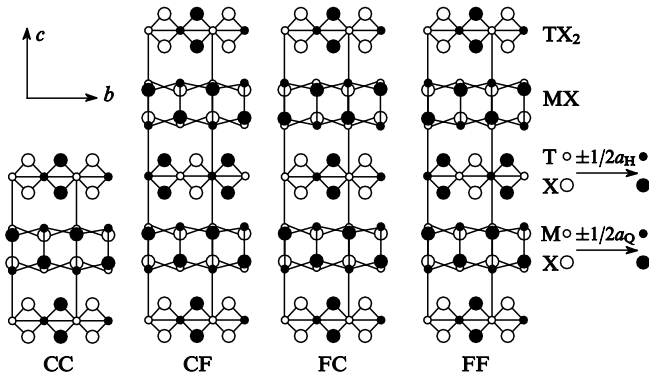


Figure 5. Different structural types of layered misfit compounds based on NbS_2 and TaS_2 (projections along the [100] direction).[5]

Table 1. Limiting stoichiometric ratios for the unit cells of some layered misfit compounds.

Compound	a_Q /Å	a_H /Å	$x = 2a_H/a_Q - 1$	$b_Q = b_H$ /Å	Ref.
$(SnS)_{1.17}NbS_2$	5.673	3.321	0.1708	5.751	24
$(LaS)_{1.14}NbS_2$	5.828	3.310	0.1359	5.797	17
$(PbS)_{1.18}TiS_2$	5.800	3.410	0.1755	5.881	21

several polytypes in the suprastructure, which hinders the formation of single crystals, and by the difference in morphology of crystalline particles of these suprastructures. Thus it was found that the synthesis and prolonged annealing (required for the attainment of thermodynamic equilibrium) of the misfit compounds $(BiS)_{1+x}(NbS_2)_m$ and $(PbS)_{1+x}(NbS_2)_m$ gave rise both to the usual layered crystals and species with the same composition, which resemble an insulation tape bundle.[11,15] Beginning with a particular diameter of the species, the layers are twisted and the maximum radius of the bundle does not exceed 0.1 mm.

III. Physical properties of misfit suprastructures

The complexity of incommensurate suprastructures (in particular, layered misfit structures) and the characteristic features of interactions between their constituent substructures result in the diversity of the physical properties observed. Misfit structures are studied by different physical and physicochemical methods. The electrophysical and magnetic properties of misfit compounds were examined in a large number of studies. The superconductivity of compounds based on some layered dichalcogenides with the 2*H* structure was also investigated. Valuable information on the physical properties of incommensurate suprastructures was also obtained in studies of X-ray photoelectron spectra, optical reflectance and Raman spectra as well as in studies with the use of some other methods.

1. Electrophysical properties

Misfit compounds containing NbX_2 or TaX_2 as the host substructure possess metallic conductivity.[11,13,19,23–26] In these structures, the resistivity (ρ_{ab}) in the *ab* plane is $\sim 10^{-6}$ Ω.[19,23–27] The ratio between the resistivities along the commensurate (*b*) and incommensurate (*a*) axes (ρ_a/ρ_b) is close to unity [for example, in the compound $(CeS)_{1.16}NbS_2$].[27] This is also evident from the number of charge carriers along the *a* and *b* axes calculated for the suprastructure $(PbS)_{1.13}TaS_2$. These values were determined from optical reflectivity measurements.[28] The resistivity along the *c* axis is substantially larger than that in the *ab* plane. The ρ_c/ρ_{ab} ratio is equal to 50 for compounds based on chalcogenides of rare-earth elements[27] and it is even larger for suprastructures with M = Sn, Pb or Bi. Thus the ρ_c/ρ_{ab} ratio for $(SnS)_{1.18}NbS_2$ is 250 and 800 at 300 and 4 K, respectively[3] ($\rho_c/\rho_{ab} \simeq 10^5$ determined at 300 K for this compound previously[24] is, apparently, overestimated).

Like some intercalates based on tantalum and niobium dichalcogenides, misfit suprastructures formed from TaS_2 or NbS_2 and PbS, SnS or BiS are characterised by a positive Hall coefficient and a negative Seebeck coefficient.[23–26] The number of holes calculated from the Hall coefficients at 4 K[25,26] suggest the occurrence of electron transfer from the MX layers to the TX_2 layers in incommensurate suprastructures, as in intercalates, the d_{z^2} band of the TX_2 layer being more than half-filled. Taking into account the negative Seebeck coefficients, it should be noted that these data are only tentative.

Suprastructures consisting of TaX_2 or NbX_2 layers and layers of REE chalcogenides are characterised by a substantially lower concentration of charge carriers compared to suprastructures containing Sn, Pb or Bi chalcogenides. These compounds possess positive Hall and Seebeck coefficients,[29–31] which is indicative of p-type conductivity in these compounds. The calculated degrees of electron density transfer in suprastructures with M = REE are

substantially higher than those observed in compounds with M = Sn or Pb.[31] The X-ray photoelectron specra of these compounds [32–35] also revealed an essential electron transfer from MX to TX_2 layers. In this case, the M atoms exist virtually in the trivalent state.

Metallic conductivity is also typical of suprastructures $(MS)_{1+x}(TiS_2)$ with M = Sn or Pb.[11,36,37] The temperature dependences of ρ_{ab} observed for $(MS)_{1+x}(TiS_2)$ [36] is analogous to those found for the intercalates Li_xTiS_2 (see Ref. 38) and Ag_xTiS_2.[39] The Hall coefficient of the former is negative and corresponds to the partial filling of the conduction band of the TiS_2 substructures by electrons from the MX substructure. However, the character of the temperature dependence of ρ_{ab} indicates that holes in the valence band of MX are not involved in the conductivity. It was thus suggested [5] that holes are localised in the valence band of the MX substructure. This localisation occurs either due to a change in the lattice potential along the [100] direction giving rise to centres of hole localisation or due to the presence of defects and vacancies in the MX sublattice.

The compounds $(CeS)_{1.19}(TiS_2)_m$ ($m = 1$ or 2) [37] also possess metallic conductivity and exhibit antiferromagnetic ordering at 2.8 K, which is not accompanied by anomalous behaviour of the conductivity around this point. This indicates that the MX layers do not contribute to the conductivity of the above-mentioned compounds. The residual resistivities observed for the compounds $(CeS)_{1.19}(TiS_2)_m$ ($\sim$ 450 and 350 μΩ cm for $m = 1$ and 2, respectively) are larger than that for Li_xTiS_2 (see Ref. 38) whose structure is not incommensurate. The authors believed that this fact is indicative of a substantial effect of the incommensurability of misfit structures on the crystal lattice, which is manifested in its local modulations playing a significant role in scattering of charge carriers.[37]

The majority of compounds with the VX_2 sublattice, for example, $(PbS)_{1.12}VS_2$ (see Ref. 12) and $(LnS)_{1+x}VS_2$ (see Refs 37 and 40) (Ln = La, Ce, Nd or Sm), exhibit semiconducting properties. It was found that the conductivity of the compounds $(LnS)_{1+x}VS_2$ (Ln = La, Ce, Pr or Nd) changed from semiconducting to metallic at 150–200 K.[41]

The V–V distances in the misfit compound $(PbS)_{1.12}VS_2$ possessing semiconducting properties [42] are close to those in the intercalates Na_xVS_2,[43] which exhibit metallic conductivity. Therefore, the semiconducting properties of $(PbS)_{1.12}VS_2$ demonstrate that holes in the valence band of PbS are not involved in the conductivity. These holes are either localised or absent due to lattice defects. X-ray structural analysis of the compound $(LaSe)_{1.21}VSe_2$ within four-dimensional symmetry space groups [44] established that the LaSe sublattice contains $\sim$ 5% of lanthanum vacancies and the VSe_2 sublattice is characterised by a large modulation of the V–V distances giving rise to centres of localisation of charge carriers. Therefore, holes available in the valence band of LaSe layers do not contribute to the conductivity of the compound $(LaSe)_{1.21}VSe_2$. Based on the conductivity data, the temperature dependence of the thermoelectric power and the optical reflectivities for the compound $(LaS)_{1.16}VS_2$, it was concluded that charge carriers are localised in LaS layers.[37]

Misfit suprastructures with the CrS_2 host substructure were prepared only for REE. The measurements of the conductivity of $(GdS)_{1.27}CrS_2$ (see Ref. 45) demonstrated that this compound exhibits semiconducting properties; the activation energy is 0.34 eV. The suprastructure $(LaS)_{1+x}CrS_2$ also possesses semiconducting properties.[45,46] The X-ray photoelectron spectra and magnetic measurements performed for the compounds $(LnS)_{1+x}CrS_2$ demonstrated that chromium atoms occupying the CrS_2 sublattice points exist in the trivalent state,[47,48] which is indicative of a substantial electron transfer from LnX layers to CrS_2 layers. In this case, a portion of electrons (x) does remain in the LnX sublattice, which seemingly should give rise to metallic conductivity in these misfit compounds (at least, for elements of the first part of the REE series whose electrons are delocalised over 5*d* and 4*f* orbitals). However, the precise chemical analysis of the compound $(LaS)_{1+x}CrS_2$ (see Ref. 45) demonstrated that the lanthanum content in this compound is less than that expected. Based on the results of the analysis, the formula $(La_{0.94}[]_{0.06}S)_{1.2}CrS_2$ was assigned to the compound $(LaS)_{1+x}CrS_2$ because the charges of La^{3+}, Cr^{3+} and S^{2-} can be balanced out only if lanthanum vacancies are present in the LaS layers. An analogous situation was observed for the compound $(GdS)_{1.27}CrS_2$ to which the composition $(Gd_{0.91}[]_{0.09}S)_{1.27}CrS_2$ was assigned on the basis of the data from precise chemical analysis and X-ray structural analysis. In this case, charge balance between the ions is observed. Therefore, the semiconducting character of the compounds under consideration is attributable to partial localisation of electrons in the MX layers.

2. Magnetic properties

The magnetic properties of layered misfit compounds based on TaX_2 or NbX_2 with the LnX guest substructure are determined primarily by the nature of the Ln atom. The strong effect of the crystal field was observed for mono- and bilayer misfit structures with M = Ce or Nd.[19,27,34,49] Studies of the magnetic properties of the compounds $(LnS)_{1+x}(TS_2)_m$ (T = Ta or Nb) demonstrated that these properties are substantially different in the directions perpendicular and parallel to the magnetic field (the direction of the field coincides with the *c* axis of the crystal). Thus the magnetic susceptibilities for the phases '$NdNb_2S_5$' and '$SmNb_2S_5$' along the field and in the transverse direction differ by factors of 1.5 and 2.5–2.6, respectively.[19] The small magnetic moments of the compounds $(LaX)_{1+x}(TX_2)_2$ (see Refs 19, 49 and 50) indicate that lanthanum atoms exist in the trivalent state, which is indicative of a substantial electron transfer from LaX layers to TX_2 layers. In suprastructures with M = Ce [51] or Sm,[34] the electron density transfer from MX layers to TX_2 layers is somewhat smaller than that observed in suprastructures with M = La. According to the results of measurements of magnetic moments, weak ferromagnetic interactions occur within the LnX layer and even weaker antiferromagnetic interactions occur between the LnX layers. At low temperature, antiferromagnetic ordering is observed in suprastructures (in this case, the temperature dependence of the magnetic moment does not obey the Curie–Weiss law).[19,38,45] For the suprastructure '$GdNb_2S_5$', the ordering occurs at 5 K.[19] For the suprastructure $(GdS)_{1.21}NbS_2$, the ordering occurs at 12.8 and 4.6 K.[38] Somewhat different results were obtained for compounds with M = Tb, Dy or Er. At low temperature, these compounds behave as paramagnetics and do not exhibit the anisotropy of magnetic properties.[5,19] This was attributed to the absence of the effect of the crystal field in the case of REE atoms located in the right part of the Periodic system due to a larger contraction of their 4*f* orbitals.

The magnetic properties of the suprastructures $(LnS)_{1+x}VS_2$ also substantially depend on the nature of the Ln atom [40,52] and are in many respects similar to the properties of the corresponding structures based on NbX_2. However, the properties of the former compounds are distinguished by stronger antiferromagnetic interactions between LnS layers. The deviation of the temperature dependence of the magnetic moment from the Curie–Weiss law at low temperatures is attributed to the effect of the crystal field. The magnetic properties of the compounds $(LnS)_{1+x}VS_2$ indicate that the Ln atoms in these compounds exist in the trivalent state.

The magnetic behaviour of misfit structures containing CrS_2 layers is more complex because of the contribution of Cr^{3+} ions.[45,47,48] Thus the compound $(LaS)_{1.20}CrS_2$ behaves as a paramagnetic up to 110–300 K. At low temperatures, two magnetic transitions (at 120 and 70 K) are observed for this compound.[48] Such behaviour of $(LaS)_{1.20}CrS_2$ is conditioned by the spins of the Cr^{3+} ions. The results of magnetic measurements for structures containing CrS_2 layers were interpreted taking into account the type of ordering of the magnetic structure at low temperature and possible antiferromagnetic interactions between the Cr ions in the CrS_2 layer (depending on the Cr–Cr distance) (see, for example, the review [5]).

3. Superconductivity

Of the known misfit suprastructures, only the compounds $(MX)_{1+x}(TX_2)_m$ (M = Sn, Pb, Bi or Ln; X = S or Se, m = 1 or 2) based on layered tantalum or niobium dichalcogenides, which have 2*H* structures and possess their own superconductivity, exhibit superconducting properties. The superconducting transition critical temperatures (T_c) for all these misfit compounds are lower than those for the corresponding dichalcogenides TX_2, which is, apparently, attributable to the insulating properties of MX layers.[53–58] For example, the T_c values for the compounds $(PbS)_{1.14}(NbS_2)_2$ and $(PbS)_{1.14}NbS_2$ are 3.4[54] and 2.475 K,[53] respectively, whereas T_c for 2*H*-NbS_2 is 6.3 K.[5] Misfit compounds based on TX_2, like dichalcogenides as such, exhibit anisotropy of the critical field, which depends on the nature of the metal M. Thus the anisotropy is $\sim$ 1.29 and 35 for $(BiSe)_{1.10}NbSe_2$ and $(LaSe)_{1.14}NbSe_2$, respectively. For mono- and bilayer suprastructures, the critical fields also have differing anisotropy. For the monolayer compounds $(SnS)_{1.17}NbS_2$ and $(PbS)_{1.14}NbS_2$, the anisotropy is $\sim$ 8–10,[53,56] whereas the anisotropy for the bilayer compound $(PbSe)_{1.12}(NbSe_2)_2$ is $\sim$ 4–5.[54] Based on the fact that the compound $(PbSe)_{1.12}(NbSe_2)_2$ exhibits anisotropy intermediate between those of $(PbS)_{1.14}NbS_2$ and $NbSe_2$ as such, it was suggested that the compound $(PbSe)_{1.12}(NbSe_2)_2$ is a second-stage intercalate.[57]

* * *

To sum up the discussion of the physical properties of layered misfit structures, it should be stated that these properties can be described to a first approximation by an additive scheme, *viz*., as a result of superposition of the properties of the TX_2 and MX substructures. Thus studies of a number of misfit structures by X-ray photoelectron and Raman spectroscopy[21,59–62] demonstrated that these spectra can be described as a superposition of the spectra of the MX and TX_2 substructures.

In some respects, this is also true for the results of studies of the electrophysical properties of these compounds. When describing suprastructures $(MX)_{1+x}(TX_2)_m$ within the framework of the rigid band model, one can use the fact that the TX_2 and MX layers in these structures are similar to the corresponding layers in crystals of TX_2 and MX, with the difference that the Fermi level for the TX_2 layer of the misfit structure is located higher than that in the crystal of TX_2 and taking into account that the changes in the MX layer compared to the analogous layer in the crystal are caused by the electron transfer to the TX_2 layer. (The charge transfer from the MX layers to the TX_2 layers was quantitatively evaluated based on the Hall and Seebeck coefficients.)

Needless to say the real situation goes beyond the scope of the simple additive scheme. For example, as mentioned above, the mutual effect of two substructures, which is manifested, in particular, in distortions and discontinuities of the crystal lattices of the TX_2 and MX layers, cannot be ignored. On the whole, the data on the physical properties of layered misfit structures confirm the correctness of their comparison with intercalates of the A_aTX_2 type.

IV. Interactions of substructures and phase stabilities of layered misfit compounds

In this Section, we consider the nature of the interaction between substructures and the possibility of deformation of their lattices. In our opinion, it is worthwhile to perform a comparative analysis of conditions of the occurrence of layered misfit structures $(MX)_{1+x}(TX_2)_m$ and intercalates A_aTX_2 (A is any metal) because this analysis can be based on the use of a unified approach determining the limits of the phase stability of the layered TX_2 host matrix. Although intercalates, unlike misfit structures, do not imply incommensurability between the host and guest lattices (in the theory of intercalates,[63] it is assumed that cavities in the host lattice topotactically correspond to the structure of the guest), both layered misfit structures and intercalates are characterised by Q–H interactions of the same type determined by charge transfer from MX to TX_2 and from A to TX_2, respectively.[64,65] The concept describing the conditions of phase stability of layered intercalates is based on the rigid band model.[66]

Depending on the coordination of the T atom, the TX_2 matrix can exist in two structural modifications related to the electronic stabilisation of the conduction bands, *viz.*, 1*T* (octahedral coordination) and 2*H* (trigonal-prismatic coordination). The schemes of the conduction bands for layered dichalcogenides of Groups IV–VI transition metals are shown in Fig. 6.

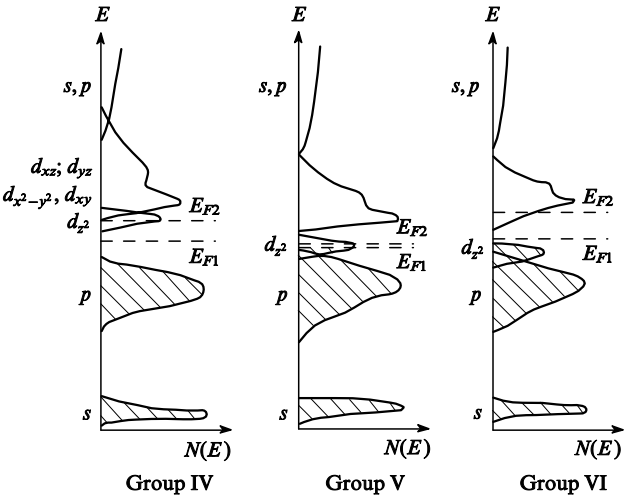


Figure 6. Band structures of transition metal dichalcogenides TX_2 (2*H* polytype).[66]

It was found[66] that the valence band of the TX_2 layer consists of two subbands to which the *s* and *p* atomic orbitals (AO) of chalcogen X make the major contributions, whereas the conduction band consists primarily of nonbonding *d*-AO of the transition metal T. The splitting of the conduction band by the crystal field of the X atoms determines its occupation by electrons and the energetics. In the 2*H* structures of TX_2, the band formed by the d_{z^2}-AO of the T metal has the lowest energy.

For the d^1 ions of Group V metals (for example, for Nb and Ta), this band is half-filled; the occupied and unoccupied levels of this band are not separated due to which these compounds exhibit metallic conductivity. Within the limits determined by the filling of the d_{z^2}-AO of the T atom, intercalation of the structures 2*H*-NbX_2 and 2*H*-TaX_2 does not lead to electron destabilisation of the system and occurs rather readily. We have demonstrated[67,68] that destabilisation of the conduction band in the intercalates Ga_aNbSe_2 and Ga_aTaSe_2 occurs at $a \approx 0.12$ and is accompanied by the transformation of a two-dimensional structure into a three-dimensional (spinel) structure, which is associated with a change in the valence states of gallium and niobium (tantalum) atoms caused by charge transfer from gallium to niobium (tantalum).

Layered misfit structures $(MX)_{1+x}(TX_2)_m$ based on dichalcogenides of Group V transition metals have been rather well studied. It was demonstrated that the degree of charge transfer from M to T depends on the properties of the MX guest layer.[17,19,25,26,29–35,49–51,62,64] In suprastructures containing lanthanide (M = Ln) sulfides (selenides) as the guest, substantial charge transfer was observed. Thus based on the temperature dependence of the conductivity and the data from X-ray photoelectron spectroscopy, it was established that the filling of the d_{z^2} band in 2*H*-TaX_2 for monolayer structures is 1.8–1.97 electrons per T metal atom. A different situation occurs in misfit compounds with M = Sn or Pb. In the latter, the charge transfer is

significantly smaller. According to the published data,[24, 25, 64] the charge transfer in these suprastructures is 0.3–0.5 electrons per T atom.

Apparently, suprastructures with T = V are a special case.[12, 37, 40, 44, 52, 61] In the phases $(PbS)_{1.12}VS_2$,[12] $(LnS)_{1+x}VS_2$ (Ln = La, Ce, Nd or Sm)[37, 40] and $(LaSe)_{1.12}VSe_2$,[44] vanadium atoms are in an octahedral environment. In these structures, as in compounds with T = Nb or Ta, electron density is transferred from MX layers to VX_2 layers, this transfer being particularly significant for compounds with M = Ln.[40, 52] As mentioned above, the V–V distances in these misfit structures are close to those in intercalates Na_xVS_2 (see Ref. 43) possessing metallic conductivity. A consideration of the electronic structures of misfit suprastructures based on VX_2 within the framework of the rigid band model assumes that these structures possess metallic conductivity. However, most of the suprastructures synthesised based on vanadium chalcogenides are actually semiconductors. This behaviour may be attributed either to the formation of an energy gap in the Fermi level due to splitting of the t_{2g} orbitals[37] or to localisation of charge carriers in the MX layer at defects of different types[37, 44, 61] caused primarily by the incommensurability of substructure lattices.

Layered matrices based on chalcogenides of Group VI metals, such as Mo and W, belong to the 2*H* polytype and are high energy-gap semiconductors. The d_{z^2} band in chalcogenides of Group VI metals with the 2*H* structure, unlike that in chalcogenides of Group V metals, is completely filled. The energy gap between this band and the nearest unoccupied levels is ~ 1.5 eV.[66] Hence, intercalation of these compounds with A donors is very hindered. Therefore, it is reasonable that layered misfit structures based on 2*H* layers of MoX_2 or WX_2 are as yet unknown. At the same time, misfit compounds based on chromium sulfide, *viz*., $(LnS)_{1+x}(CrS_2)_m$, with the 1*T* structure of the host matrix have been characterised in sufficient detail. These compounds are semiconductors with an energy gap of ~ 0.5 eV. In these compounds, as in the compounds $(LnS)_{1+x}(VS_2)_m$, the M and T atoms exist in the trivalent states due to a substantial charge transfer from Ln to Cr and the presence of vacancies in Ln positions.[37, 45, 46]

Layered misfit suprastructures with M = Bi or Sb are a special case. Although these compounds are very similar in structure and properties to compounds with M = Pb or Sn, the charge transfer in the former compounds determined from electrophysical data[23, 26] is substantially smaller than that in misfit structures with M = Pb or Sn, unless a strong acceptor, such as CrS_2, serves as the host matrix.[64] The X-ray photoelectron spectra[69] of the compounds $(SbS)_{1+x}CrS_2$ and the Bi–S bond lengths in $(BiS)_{1.23}CrS_2$ (see Ref. 70) demonstrate that the Sb and Bi atoms in these compounds exist in the trivalent state. A number of characteristic structural features of the compounds $(BiS)_{1.08}TaS_2$ and $(BiSe)_{1.09}TaSe_2$ containing short Bi–Bi bonds were mentioned.[15]

Of Group IV transition metals, only titanium atoms form layered dichalcogenide structures with a crystal lattice of the 1*T*-CdI type (with octahedral coordination about the T atom, see Fig. 3). Generally, their intercalation with donors (metals) is accompanied by a $1T \rightarrow 2H$ phase transition.[63] The atomic t_{2g} orbitals of titanium ions with the d^0 electronic configuration are unoccupied. However, intercalation of the TiX_2 matrix with A donor atoms leads to the electron transfer from A atoms to Ti ions and to the occupation of the t_{2g} orbitals. In this case, their degeneracy is eliminated because the trigonal-prismatic (2*H*) coordination about Ti atoms with the lower-energy d_{z^2} band becomes energetically more favourable. A rather surprising thing is that the Ti atoms retain an octahedral coordination in spite of the difference in the character of the MX layers and the conditions of charge transfer.

Titanium dichalcogenides form layered misfit compounds with Pb, Sn,[11, 21, 36, 61, 71, 72] Ce[37] or Ag.[73] Electrophysical measurements[36, 37] and analysis of photoelectron spectra[21, 61, 74, 75] and Raman spectra[61] indicate charge transfer from MX layers to TiX_2 layers. The nature and bond strengths between the layers in such misfit structures were interpreted differently. Thus, in some studies[3, 64, 69] it was assumed that the MX and TiX_2 layers are covalently bound (*viz*., that there are covalent bonds between the M atoms of the MX layers and the X atoms of the TiX_2 layers). In other studies, it was reported that there are Coulombic interactions between the positively charged metal atoms M from the MX layers and the negatively charged chalcogen atoms from the TX_2 layers, as, for example, in the compounds $(PbS)_{1.18}(TiS_2)_m$ (m = 1 or 2). Electron probe microanalysis of this compound[71] revealed a deficiency of lead ions in the PbS layers, which was interpreted as the replacement of 8%–10% of Pb^{2+} ions by Ti^{3+} ions, which may lead to stabilisation of the misfit suprastructure. The stability of the compounds $(CeS)_{1.19}(TiS_2)_m$ (m = 1 or 2) was estimated within the framework of the rigid band model based on the results of measurements of the electrical resistivity, thermoelectric power and optical reflectivity.[37]

However, the results of the majority of studies, in our opinion, indicate that the interaction between the MX and TX_2 substructures occurs through charge transfer from the MX layers to the TX_2 layers. For example, calculations of the band structure of $(LaS)(SrS)_{0.2}CrS_2$ demonstrated[46] that there is no more or less significant charge density between the lanthanum atoms from the LaS layer and the sulfur atoms from the CrS_2 layer. On the contrary, the lone electron pairs of the sulfur atoms of the CrS_2 layer are directed toward the free space rather than toward the lanthanum atoms of the adjacent layer. In this case, the factors determining the polytype of the TX_2 layer in the resulting suprastructures remain unclear. In our opinion, the energy characteristics of the structures under consideration play here a decisive role. These characteristics can be described based on the concept of electronic stabilisation of the suprastructure. This concept was confirmed by the results of the study[45] in which the formation of defects in MX substructures due to the transfer of an excess charge from the MX layer to the TX_2 layer was experimentally observed and theoretically justified.

One would expect that intercalation of layered misfit structures with donor species will be accompanied by phase transitions associated with changes in substructures. Analogous processes were observed, for example, on the formation of intercalates of the A_aTX_2 type.[67, 68] The formation of defects (discontinuities) in the MX substructure may be yet another consequence of intercalation.

As mentioned above, intercalates based on layered misfit compounds are formed due to charge transfer and filling of unoccupied levels of the suprastructure. Unfortunately, examples of the existence of such intercalates, their structural features and properties are limited in number. However, to a first approximation it can be stated that the rule of electronic stabilisation is fulfilled for these compounds, as in the case of intercalation of typical layered matrices. At the same time, it is important to keep in mind the differences associated with the charge transfer in the above-mentioned intercalates and in the corresponding misfit structures. Studies of intercalation of the suprastructures '$PbVS_3$', '$PbTiS_3$', '$PbTi_2S_5$' and '$SnTiS_3$' with lithium (from solutions of n-butyllithium in hexane at room temperature)[14] demonstrated that intercalation of monolayer misfit structures occurs with greater difficulty than that of the corresponding bilayer structures. Analogous results were obtained in the study[76] in which the electrochemical intercalation of the compounds $(PbS)_{1.18}TiS_2$ and $(PbS)_{1.18}(TiS_2)_2$ with silver was examined. It was demonstrated that the insertion of silver into the structure $(PbS)_{1.18}TiS_2$ resulted in disproportionation of the latter into $Ag_x(PbS)_{1.18}(TiS_2)_2$ and PbS.

Similar results were obtained upon intercalation of iron and nickel into layered misfit structures based on TiS_2 and LaS or CeS.[77] Monolayer intercalates could not be prepared, whereas the bilayer structures of the $A_a(LaS)_{1.18}(TiS_2)_2$ type were synthesised and studied. Presumably, the formation of intercalates (in the case

of a comparable donor ability of the intercalant) becomes easier as the charge transfer from MX to TX_2 decreases and as the electron 'capacitivity' of the unoccupied band is increased. In this respect, the probability of intercalation of layered misfit compounds possessing the $1T$ structure is higher than that of compounds with the $2H$ structure because a metal atom with octahedral coordination can accept a larger number of electrons than an atom with trigonal-prismatic coordination.

Intercalation of metals into the synthetic matrix $Ta_{1-x}Re_xSe_2$ was also studied.[78,79] The electronic structure of this matrix can be changed by varying its composition, *i.e.*, by varying the x value. For $x = 0.5$, this matrix is isoelectronic and isostructural to the matrix $2H$-$MoSe_2$, *viz.*, the d_{z^2} band in this matrix is filled and intercalation is accompanied by disproportionation of the layered structure.

The results of a study[46] in which the possibility of the replacement of a portion of lanthanum atoms in $(LaS)_{1+x}CrS_2$ by 'inert' Sr was examined can be cited as supporting evidence for the above concept of electronic stabilisation. The results obtained demonstrated that the structure $(LaS)_{1+x}CrS_2$ contains a substantial amount (~ 0.2) of lanthanum vacancies, *i.e.*, the corresponding suprastructure is a nanocomposite. This fact was indirectly confirmed by the results of another study,[16] where it was attempted to obtain images of LaS layers in the suprastructure $(LaS)_{1.14}NbS_2$ by scanning tunnelling electron and atomic-force microscopy; however, the attempts were unsuccessful.

Probably, the differences in the morphology of the synthesised crystalline species $(BiS)_{1+x}(NbS)_m$ are also associated with the conditions of the interaction between the constituent substructures. Among the specimens obtained, layered structures as well as structures of the 'insulation-tape bundle' type were found. As mentioned above, no noticeable electron density transfer was observed in layered misfit structures with M = Bi or Sb, unlike those with M = Ln. In the case of the former stuctures, single crystals are deformed and take the shape of an 'insulation-tape bundle' or a bent tube (because stresses due to the incommensurability of the layers in one direction result in the curvature) due to the incommensurability of the intercalant MS and the nonrigidity of the TS_2 matrix.[80–82] The optimum inner and outer radii of 'bundles' are determined by the force balance retaining the matrix rigidity as well as by the conditions of the interaction between substructures.

Unfortunately, data on the thermodynamic properties of layered misfit structures are lacking in the literature. We suggested that the formation of defects (discontinuities) in intergrowth incommensurate substructures and the degree of additivity of the substructure contributions to the observed properties of the suprastructure can be studied by thermal analysis and differential scanning calorimetry.

We established that the specific heats of the compounds $(SnS)_{1+x}TaS_2$ and $(PbS)_{1+x}TaS_2$ cannot be described in the context of the additivity. Anomalies were also found for the temperature dependence of the specific heat due to first-order phase transition. Thus it was demonstrated that compounds with the nonextreme stoichiometry ($x = 0$) did not give a low-temperature (35–70 °C) specific-heat peak, whereas these peaks for quenched and nonquenched samples of $(SnS)_{1.15}TaS_2$ differ in height. For all compounds based on TaS_2, the specific-heat peak was observed at 350 °C. The peak height depends on the stoichiometry and the conditions of cooling of the samples. Probably, these effects are associated with disruptions in one of the sublattices.

Our studies demonstrated that the compounds $(SnS)_{1+x}TaS_2$ actively decomposed at above ~ 600 °C in an inert atmosphere to liberate elementary sulfur. Apparently, the intercalates Sn_xTaS_2 were the final decomposition products. In the future, we hope to confirm the fact that the observed phase transitions are associated with discontinuities in one of the sublattices (MX). In our opinion, these compounds are thermodynamically unstable due to the effect of the incommensurability on the crystal structure. Apparently, strengthening of the interaction between substructures (for a given incommensurability) leads to an increase in the instability of the suprastructure due to a change in the energy of the bonds between the metal and chalcogen atoms in one of the substructures.

We have presented sufficiently convincing evidence for the possibility of fragmentation of one of the sublattices in the misfit structure $(MX)_{1+x}(TS_2)_m$. The equation of motion was solved within the framework of the Frenkel–Kontorova model taking into account the anharmonicity of the elastic sublattice and the incommensurability between the period of this sublattice and the corresponding lattice parameter of the crystal environment. The corrections for the known solutions of the equation of motion in the harmonic approximation were also found. It was demonstrated that under conditions of anharmonicity of the interaction between the sublattice and the host lattice, two reasons for its possible fragmentation into particles of finite length exist, *viz.*, the incommensurability and doubling of the period of solutions of the nonlinear problem describing this model. The solution obtained determines the conditions of formation of one-dimensional nanocomposite structures and the limiting parameters at which the suprastructure of the ensemble changes from regular to random.

V. Conclusion

Incommensurate suprastructures, which have been studied thus far, are limited only to compounds in which one lattice parameter of intergrowth substructures is incommensurate (a one-dimensional case). Apparently, eutectics can serve as abundant examples of suprastructures characterised by incommensurability along all three crystallographic directions. As it usually is, the transformation from a one-dimensional model to a three-dimensional system, presents problems. However, it can be said that some general criteria for the formation of suprastructures with the three-dimensional incommensurability were revealed.

First, it is apparent that the incommensurability of intergrowth substructures in real suprastructures occurs within particular limits. Apparently, for some incommensurability parameters, the interaction between sublattices can lead to the formation of defects of different types, including fragmentation of one of the substructures. We failed to find literature data on the dependence of the properties and structures of layered misfit structures on the incommensurability. However, it is apparent that the character of the interaction between substructures should depend on the stoichiometric ratio, *i.e.*, on the x and m values. As mentioned above, indirect evidence is available for the fact that monolayer structures undergo disproportionation to form bilayer and simple structures as the x parameter changes (see the data on intercalation of misfit structures[14,76,77]). Other data (tubular morphology of particles,[15] the results of studies by scanning tunnelling electron and atomic-force microscopy[70] and results of our investigations of thermodynamic properties of misfit structures) indicate that defects in substructures comprising the misfit structure or in one of these substructures are frequently observed.

Second, it was proved that it is important to meet the conditions of electronic stabilisation of suprastructures. Since the charge transfer is the major mechanism responsible for the interaction between structural elements in misfit suprastructures, the conditions of electronic stabilisation determine both the stabilities of substructures and the existence of a suprastructure as a whole. The above-considered differences in the character of the interaction between substructures MX and TX_2 determine both the possibility of formation of defects in the substructures and their character [see the data[44,45,69] on the structures $(LaS)_{1+x}CrS_2$, $(LaSe)_{1+x}VSe_2$ and $(PbS)_{1+x}TiS_2$]. The differences in the morphology of misfit particles are also attributable to these facts.[15]

Third, it was established that the nonrigidity of substructures is of importance, at least it was demonstrated that deformations of sublattices due to their incommensurability should be taken into

account both in structural studies and in investigations of physicochemical properties of incommensurate compounds. For example, it can be suggested that bonds in one sublattice can be cleaved at particular tensile stresses and new bonds in another sublattice can be formed at particular compression stresses. The latter possibility is supported by the results of the study of the structures $(BiS)_{1.08}TaS_2$ and $(BiSe)_{1.09}TaSe_2$ [15] in which short (as in metals) Bi—Bi bonds were found. The results of the study [16] provided indirect evidence for the cleavage of bonds in MX substructures.

Finally, approaches and procedures, which allow one to determine the conditions of fragmentation of substructures, were theoretically justified.

In the present review, we call attention to some apparent relationships responsible for the structural characteristics, structure imperfection and morphology of particles of crystalline suprastructures formed from incommensurate elements. Although it is evident that this problem is of importance in solid-state chemistry and in many fields of materials science, it has not been discussed previously in the literature.

Evidently, three situations can occur upon formation of incommensurate intergrowth suprastructures. In the first case, the nonrigidity of the lattices compensates for their insignificant incommensurability. In this case, the formation of a suprastructure is accompanied by stresses, but it does not disturb the stoichiometry. In the second situation, rigid substructures exist and the interaction between these substructures are rather weak. In this case, rather well-organised crystalline suprastructures are formed at any incommensurability. Their limiting stoichiometry is determined by the incommensurability, and the properties, most likely, additively depend on the properties of the constituent elements. The third situation is associated with mechanisms of structural compensation. Due to the strong interaction between substructures, their nonrigidity and substantial incommensurability, discontinuities can appear in one of the sublattices accompanied by the formation of nanocomposites. The structural compensation of the resulting stresses may lead to the formation of unusual defects or give rise to an unusual morphology of particles of suprastructural aggregates. It is also possible that particular limitations on the particle sizes occur. The last-mentioned situation is based on rather abundant experimental data. In our opinion, this situation is of prime interest within the framework of the problems under consideration.

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