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Semiconducting clathrates: synthesis, structure and properties

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Abstract. The review surveys different aspects of chemical studies of semiconducting clathrates belonging to a unique family of inclusion compounds. The classification, crystal and electronic structures, properties and methods for the synthesis of semiconducting clathrates are considered on the basis of analysis of recent publications. The prospects for fundamental research and the construction of new-generation materials based on semiconducting clathrates are discussed. The bibliography includes 161 references.

I. Introduction

The term 'clathrates' refers to compounds with a three-dimensional framework structure (host), whose cavities are occupied by isolated (in rare instances, one-dimensional infinite) associates of molecules, atoms or ions (guests), which do not form covalent bonds with the framework.[1] The crystal lattice of the host cannot exist in the absence of a guest. For the framework to be stabilised, cavities must be at least partially occupied. For this reason, clathrates are synthesised by co-crystallisation of a host and a guest. Generally, species included into a three-dimensional matrix cannot leave the latter without destruction of the overall architecture. The name 'clathrate' was first used by Powell in 1948 [2] (after the Latin word *clathratus*, which means 'enclosed or protected by cross bars of a grating'). Sometimes, the term 'clathrate' is used in a broader sense and applied not only to compounds in which the host has a three-dimensional structure (framework clathrates), but also to compounds with two-dimensional (layered clathrates or intercalates) and zero-dimensional (molecular clathrates) host structures. Examples are layered inclusion compounds of graphite and complexes of crown ethers with alkali metals. However, an extension of the term 'clathrate' to such systems is not commonly accepted.[2]

Over many years, only gas hydrates and compounds based on hydroquinone and urea have been assigned to clathrates, which have been considered as an exotic variety of inclusion compounds.[3] These compounds have attracted some interest from researchers because of their unusual structures. Certain silicates [4] and silicides [5] isostructural to gas hydrates and then germanides and stannides,[6] which were characterised in 1960 – 1980s, also aroused some interest. Only about two tens of papers have been published over the last 30 years.

The situation changed radically after the development of the Phonon Glass – Electron Crystal concept.[7] Taking into account this concept, particular inclusion compounds, which are poor conductors of heat (as amorphous compounds) and good conductors of electricity (as covalent semiconductors), can serve as a basis for the design of new-generation heat-saving materials.[8] In particular, this class of compounds includes clathrate germanides and stannides. The results of initial experiments published in 1998 [9] already confirmed that clathrates are promising new materials for thermoelectric cooling. This stimulated interest in semiconducting clathrates, as evidenced by a sharply increasing number of publications devoted to various aspects of the chemistry and physics of these compounds. In 2000, Bobev and Sevov published a brief review [10] concerned with the chemical aspects of clathrates. One year later, Nolas, Slack and Schjuman published a comprehensive review,[11] where the results of studies of the physical properties were discussed and related to the structural data.

Since that time, new types of clathrates have been synthesised. New data on the characteristic features of their crystal and electronic structures were obtained, which gave an insight into unusual transport properties of these compounds. Finally, clathrate silicides were found to exhibit superconducting properties. Therefore, the accumulated data on the crystal and electronic structures and the properties of semiconducting clathrates needed to be summarised. Our review is devoted to these problems. We consider the classification, crystal and electronic structures of semiconducting clathrates and some specific physical properties of these compounds determined by their structures. We also discuss prospects for gaining fundamental knowledge and constructing new materials.

Crystal hydrates of gases and liquids are the best known representatives of the clathrate family. Chlorine hydrate was discovered as early as 1811 by Davy, when he passed chlorine through water cooled to 2 – 3 °C.[12] In 1823, Faraday determined the composition of the new compound as $Cl_2 \cdot 10\,H_2O$,[1] which is close to the true composition $Cl_2 \cdot 7.25\,H_2O$. The crystal structure of chlorine hydrate was established by Allen as late as 1952.[13] In this compound, water molecules are linked by hydrogen bonds to form a three-dimensional framework (Fig. 1). Each water molecule is linked to four other water molecules. The framework contains polyhedral cavities. The oxygen atoms occupy the corners of these polyhedra, whereas the hydrogen atoms are

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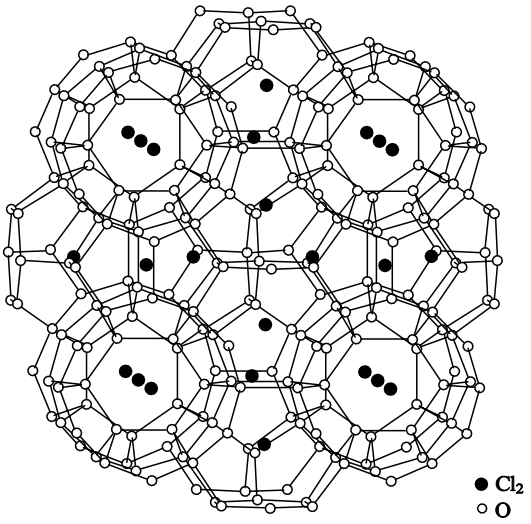


Figure 1. Crystal structure of chlorine hydrate $(Cl_2)_{6.34}[H_2O]_{46}$. Hydrogen atoms are omitted.

located at their edges. In the chlorine hydrate, there are 8 polyhedral cavities per 46 water molecules. If all cavities are occupied by chlorine molecules, the idealised formula is $(Cl_2)_8[H_2O]_{46}$. However, the true composition of the compound is close to $(Cl_2)_{6.34}[H_2O]_{46}$, and the chlorine molecules occupy cavities only partially. Strictly speaking, this compound cannot be assigned to hydrates based on its crystal structure. Nevertheless, this is the commonly accepted term, which is universally used in the literature.[1,3]

Numerous hydrates of other gases (for example, of noble gases Ar, Kr and Xe), gaseous and liquid inorganic compounds (N_2, O_2, CO_2, H_2S, PH_3, SO_2) and organic compounds [CH_4, CH_3Cl, C_2H_6, C_3H_8, $CHCl_3$, CH_3NO_2, cyclopentane, cyclobutanone, $(n\text{-}C_4H_9)_3SF$] were synthesised.[14] Clathrates in which compounds other than water (for example, phenol or hydroquinone) serve as the host are also known.[15] In all cases, the ratio of the cavity size in the host framework to the size of the guest molecules or atoms plays a decisive role in the formation of a clathrate structure, whereas the chemical nature of the guest molecules is of minor importance. Actually, small hydrogen, helium and neon molecules do not form such structures with water, whereas H_2S, PH_3, Cl_2 and Br_2, which have suitable sizes, are involved in such compounds even though they are chemically active and differ in acid-base and redox properties. It should be noted that the hydrogen hydrate can be prepared under high pressure, but the cavities in the framework formed by water molecules are occupied by clusters formed by two or four H_2 molecules, whose sizes match those of the cavities of different types.[16] All the above facts indicate that the size factor has a determining effect on the formation and stability of clathrates.

Prerequisites for the formation of clathrate structures are the presence of a host matrix built from tetrafunctional units (each unit forms four bonds within the matrix) and the ability of the corresponding guest species to occupy the cavities in the framework formed. In hydrates of gases and liquids, the host and guest atoms are formally uncharged, although it is these weak Coulombic interactions that play the major role in the stabilisation of the structure. All known hydrates crystallise in seven structural types, which differ in the type of polyhedra formed in the framework and the mode of their arrangement in the three-dimensional structure.[3]

Virtually all hydrates of gases and liquids decompose on heating, which strongly limits their application. Nevertheless, the possibility of using methane hydrate as a natural nanocrystalline container is discussed taking into account vast resources of methane, which exists as crystal hydrate on the World's Ocean Floor. There are plans to recover and transport these resources in the solid state.[17]

In addition to hydrates, there are about 120 inorganic compounds with clathrate structures, which are referred to as semiconducting clathrates. Our review is devoted to the latter compounds. In such clathrates, a three-dimensional framework is formed primarily by Group 14 elements (Si, Ge or Sn). These compounds are sometimes loosely (in our opinion) called 'intermetallic clathrates'.[18] It should be noted that the first compounds of this class, which were synthesised in the 1960s,[3] can be assigned to intermetallides because their frameworks consist of silicon atoms and the cavities are occupied by alkali metal cations. However, this is not correct for analogous compounds with pnicogens (P, As and Sb), tellurium and halogens (Cl, Br and I), which were also synthesised.[19–32] Therefore, the term 'intermetallic' can be applied only to some semiconducting clathrates. The term 'semiconducting' is also not perfect because the above compounds do not all have semiconducting properties (particular phases exhibit metallic conductivity). However, in our opinion, the term 'semiconducting' is more universal. Hereinafter, we shall use this term for all compounds of the class under consideration.

In contrast to hydrates, in which the host and guest atoms are formally uncharged, the framework and the guest atoms in semiconducting clathrates bear opposite charges. Besides, guests in semiconducting clathrates are always monoatomic. Compounds containing molecules or polyatomic ions as the guest are presently unknown.

1. Classification of semiconducting clathrates

Clathrate hydrates of gases and liquids crystallise in seven structural types, which are denoted by Roman numerals: type I clathrate, type II clathrate, ..., type VII clathrate.[3] Semiconducting clathrates crystallise only in three of these structural types, *viz.*, type I clathrate, type II clathrate and type III clathrate. Besides these, two structural types, which were not found for hydrates, are known as semiconducting clathrates. These types are referred to as the type VIII clathrate[33–35] and type IX clathrate.[36] Because of specific structural features, compounds of the latter type are sometimes called chiral clathrates.†

It should be noted that the distribution of semiconducting clathrates over the above structural types is essentially non-uniform. Almost 100 type-I clathrate compounds are known. About 10 compounds have the type-II clathrate structure, almost the same number of compounds have the type-IX clathrate structure, whereas only a few type-III clathrate and type-VIII clathrate compounds were synthesised.

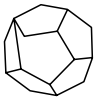
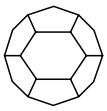
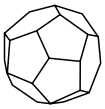
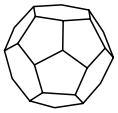
Semiconducting clathrates can alternatively be classified according to the formal charge of the framework. The polyanionic and polycationic clathrates are distinguishable.[14,38] In polyanionic clathrates, the framework bears a negative charge and the guest atoms are positively charged (cations of alkali and alkaline-earth metals and europium). The reverse situation is observed for polycationic clathrates. In these compounds, the framework bears a positive charge and the guest atoms are negatively charged (halide anions).

2. Clathrate-forming polyhedra

The crystal structures of clathrates of any type contain a three-dimensional host framework, which is formed by tetrafunctional units and contains large cavities. The cavities in the framework are polyhedra with $n \geqslant 20$ vertices and regular pentagonal and hexagonal faces.[1,10,14] The polyhedra are denoted by the number of such faces.[39] For example, the notation [5^{12}] is used for a

† In a number of publications, type VIII clathrates are referred to as type III clathrates. This is incorrect because type III clathrates belong to the structural type of bromine hydrate $(Br_2)_{20}\square_{10}[(H_2O)_{172}]$,[1] for which semiconducting analogues are also known.[37] The structures of these compounds are radically different from chiral type VIII clathrates.

Table 1. Clathrate-forming polyhedra.

Name	Graphical representation	Notation	Number of penta/hexagons	Number of vertices	Observed in clathrates
Pentagonal dodecahedron		$[5^{12}]$	$\frac{12}{0}$	20	I, II, III VIII,[a] IX
Tetrakaidecahedron		$[5^{12}6^2]$	$\frac{12}{2}$	24	I, III
Pentakaidecahedron		$[5^{12}6^3]$	$\frac{12}{3}$	26	III
Hexakaidecahedron		$[5^{12}6^4]$	$\frac{12}{4}$	28	II

[a] The type VIII clathrate contains distorted pentagonal dodecahedra.

pentagonal dodecahedron, *viz*., a 20-vertex polyhedron containing 12 pentagonal faces. The 24-vertex polyhedron (hexakaidecahedron) containing 12 pentagonal and 2 hexagonal faces is denoted by $[5^{12}6^2]$. Table 1 lists all polyhedra found in the structures of semiconducting clathrates.

A guest atom is located inside each polyhedron. The guest atom and the polyhedron are sometimes denoted by $G@E_x$.[1] This notation signifies that the guest atom G is located inside an *x*-vertex polyhedron formed by E atoms. For example, the notation $Cs@Sn_{20}$ represents the pentagonal dodecahedron consisting of tin atoms with a cesium atom inside.

The pentagonal dodecahedron is a Platonic body, in which all corners are equivalent and all faces are identical (in real structures, of the same type).[1] This polyhedron was found in the structures of clathrates of all types, except for type-VIII clathrate compounds. In the latter, the polyhedra are slightly distorted. Since the pentagonal dodecahedron has several fivefold axes, it is impossible to fill space with only these polyhedra, and it is necessary to combine these polyhedra with polyhedra which contain, in addition, hexagonal faces. Evidently, the total size of the cavity increases with increasing number of hexagonal faces, and the volumes of the polyhedra containing hexagonal faces are larger than the volume of the pentagonal dodecahedron.

II. Crystal chemistry of semiconducting clathrates

1. Type I clathrate

The type-I clathrate structure contains two types of polyhedra, *viz*., pentagonal dodecahedra $[5^{12}]$ and larger 14-face tetrakaidecahedra $[5^{12}6^2]$. The tetrakaidecahedra are linked to each other by sharing hexagonal faces to form a three-dimensional system of mutually perpendicular non-intersecting channels (Fig. 2). The pentagonal dodecahedra are enclosed in this system of channels and are isolated from each other. The unit cell contains 46 atoms of the framework and has 2 small and 6 large cavities. Therefore, the formula of the corresponding ideal clathrate is $G^{I}_2G^{II}_6[E_{46}]$ (G is a guest). All semiconducting clathrates, which crystallise in this structural type are listed in Tables 2 and 3.

Most type-I clathrate compounds crystallise in the cubic system in the centrosymmetrical space group *Pm*3*n*; 46 atoms of the framework occupy three positions, *viz*., 6*c*, 16*i* and 24*k*. The atoms in the 16*i* and 24*k* positions are present in the polyhedra of both types, whereas the atoms in the 6*c* position are present only in the bulkier tetrakaidecahedra (see Fig. 2). The atom in the 6*c* position is tetrahedrally coordinated by four atoms occupying the 24*k* position. The atom in the 16*i* position is tetrahedrally coordinated by three atoms occupying the 24*k* position and one atom occupying the 16*i* position. The atom in the 24*k* position is tetrahedrally coordinated by one atom occupying the 6*c* position, two atoms occupying the 16*i* position and one atom occupying the 24*k* position (Fig. 3 *a*).

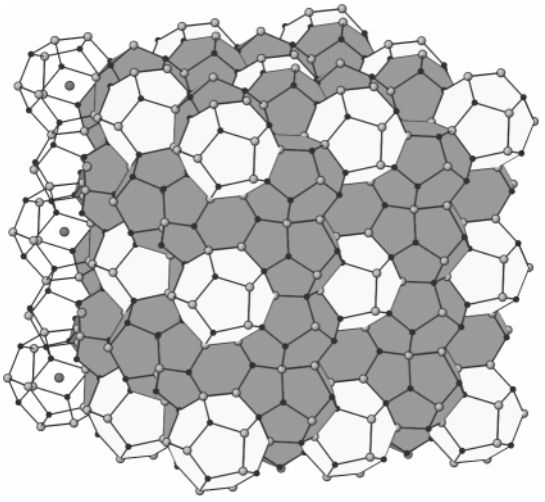


Figure 2. Polyhedral representation of the type-I clathrate structure.

In the structures of compounds of the general formula $X_8[Ge_{38}Z_8]$ (X = Cl, Br, I; Z = P, As, Sb), the centre of symmetry is absent. All these phases crystallise in the space group *P*43*n*, which is a non-centrosymmetrical analogue of the space group *Pm*3*n*.[19–21] Due to a loss of the centre of symmetry, the 16*i* position of the space group *Pm*3*n* is split into two eightfold 8*e* positions in the space group *P*43*n*. One of these positions is completely occupied by germanium atoms, whereas another one is occupied by pnicogen atoms. To our knowledge, the space

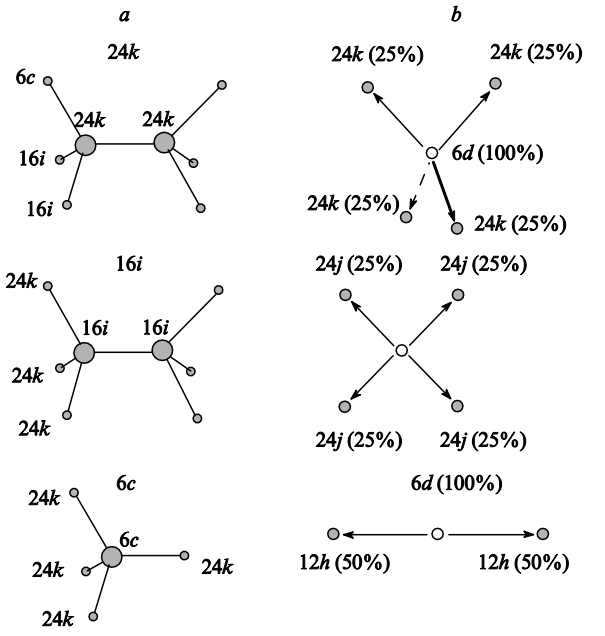


Figure 3. Atomic positions in the type-I clathrate structure. (*a*) Atoms of the clathrate framework, (*b*) disorder of the guest atoms in the 6*d* position.

Table 2. Type-I polyanionic clathrates.

Elements of the framework	Na, K, Rb, Cs as guest atoms	Ref.	Sr, Ba, Eu as guest atoms	Ref.
Compounds with a framework of silicon atoms				
p Metals	$Na_8[Si_{46}]$	3, 40 – 42	$Ba_{8-x}\square_x[Si_{46}]$	48 – 51
	$Na_{8-x}Ba_x[Si_{46}]$	43	$Ba_{7.7}\square_{0.3}[Si_{42.7}Ge_{3.1}\square_{0.2}]$	49
	$Na_xBa_6[Si_{46}]$	44	$Ba_{7.7}\square_{0.3}[Si_{39.3}Ge_{6.4}\square_{0.3}]$	49
	$K_{7.62}\square_{0.38}[Si_{46}]$	45	$Ba_{7.9}\square_{0.1}[Si_{33.3}Ge_{12.0}\square_{0.7}]$	49
	$Rb_{6.15}\square_{1.85}[Si_{46}]$	45	$Sr_8[Ga_{11}Si_{35}]$	52
	$K_8[Ga_8Si_{38}]$	46	$Sr_8[Ga_{12}Si_{34}]$	52
	$Rb_8[Al_8Si_{38}]$	47	$Ba_8[Ga_{16}Si_{30}]$	33, 47
	$Rb_8[Ga_8Si_{38}]$	46		
p and d Metals			$Ba_8[Ni_{1.8}Si_{44.2}]$	53
			$Ba_8[Pd_{2.5}Si_{43.5}]$	53
			$Ba_8[Pt_{2.7}Si_{43.3}]$	53
			$Ba_8[Cu_4Si_{42}]$	53
			$Ba_8[Ag_{3.8}Si_{42.2}]$	53
			$Ba_8[Au_6Si_{40}]$	53, 54
			$Ba_8[Au_6Si_{20}Ge_{20}]$	54
Compounds with a framework of germanium atoms				
p Metals	$K_8[Al_8Ge_{38}]$	55	$Ba_8[Ge_{43}\square_3]$	49, 61
	$Rb_8[Al_8Ge_{38}]$	56	$Ba_8[Al_{16}Ge_{30}]$	33, 47
	$K_8[Ga_8Ge_{38}]$	8	$Sr_8[Ga_{16}Ge_{30}]$	62
	$Rb_8[Ga_8Ge_{38}]$	57	β-$Eu_8[Ga_{16}Ge_{30}]$	34, 62,
	$Cs_8[Ga_8Ge_{38}]$	58		63
	$K_8[In_8Ge_{38}]$	59	$Ba_8[Ga_{4.44}Ge_{39.14}\square_{2.42}]$	64
	$Rb_8[In_8Ge_{38}]$	59	$Ba_8[Ga_{8.62}Ge_{36}\square_{1.38}]$	64
	$Cs_8[In_8Ge_{38}]$	60	$Ba_8[Ga_{12.35}Ge_{33.27}\square_{0.38}]$	64
			$Ba_8[Ga_{16}Ge_{30}]$	33, 34, 62, 65
			$Ba_8[Ga_{17}SbGe_{28}]$	66, 67
			$Ba_8[In_{16}Ge_{30}]$	68
			$Ba_8[Zn_8Ge_{38}]$	68
			$Ba_8[Cd_8Ge_{38}]$	68
			$Ba_8[Cd_4Ge_{40}\square_2]$	68
p and d Metals			$Ba_8[Ni_xGe_{46-x}]$	53
			$Ba_8[Pd_6Ge_{40}]$	53
			$Ba_8[Pt_xGe_{46-x}]$	53
			$Ba_8[Cu_xGe_{46-x}]$	53
			$Ba_8[Ag_6Ge_{40}]$	53
			$Ba_8[Au_6Ge_{40}]$	53, 54
Compounds with a framework of tin atoms				
p Metals	$K_{1.6}Cs_{6.4}[Sn_{44}\square_2]$	69	β-$Ba_8[Ga_{16}Sn_{30}]$	73
	$Rb_8[Sn_{44.6}\square_{1.4}]$	69	$K_{3.5}Ba_{4.5}[Ga_{12.5}Sn_{33.5}]$	47
	$Cs_8[Sn_{44}\square_2]$	8, 47, 70	$Ba_8Cu_{16}P_{30}$ (see[a])	74
	$K_8[Al_8Sn_{38}]$	47		
	$Rb_8[Al_8Sn_{38}]$	47		
	$K_8[Ga_8Sn_{38}]$	47		
	$Rb_8[Ga_8Sn_{38}]$	57		
	$Cs_8[Ga_8Sn_{38}]$	58		
	$Cs_8[Zn_4Sn_{42}]$	71		
	$Cs_8[Cd_4Sn_{42}]$	72		

[a] Compounds devoid of Group 14 elements.

Table 3. Type-I polycationic clathrates (halogen atoms as the guest).

Compounds with a framework of Ge atoms	Ref.	Compounds with a framework of Sn atoms	Ref.
P, As, Sb as a non-metal in the framework		P, As as a non-metal in the framework	
$I_8[Ge_{38}P_8]$	19 – 21	$I_8[Sn_{24}P_{19.3}\square_{2.7}]$	25
$Br_8[Ge_{38}P_8]$	20, 21	$Br_8[Sn_{24}P_{19.6}\square_{2.4}]$	31, 32
$Cl_8[Ge_{38}P_8]$	20, 21	$Br_xI_{8-x}[Sn_{24}P_{19.3}\square_{2.7}]$	31, 32
$I_8[Ge_{38}As_8]$	19 – 21, 23	$I_8[Sn_{14}In_{10}P_{21.2}\square_{0.8}]$	29
$Br_8[Ge_{38}As_8]$	20, 21, 23	$I_8[Sn_{10}In_{14}P_{22}]$	29
$Cl_8[Ge_{38}As_8]$	20, 21	$I_8[Sn_{17}Zn_7P_{22}]$	26, 75
$I_8[Ge_{38}Sb_8]$	20, 21	$Br_8[Sn_{17}Zn_7P_{22}]$	75
$Br_8[Ge_{38}Sb_8]$	20, 21	$I_8[Sn_{20}Zn_4P_{20.8}\square_{1.2}]$	75
$I_8[Ge_{14}Ga_{12}Sb_{20}]$	22	$I_8[Sn_{17}Cd_7P_{22}]$	75
Te as a non-metal in the framework		$I_8[Sn_{19.3}Cu_{4.7}P_{22}]$	28
$I_8[Ge_{46-x}Te_x]$	26	$I_8[Sn_{24}As_{19.3}\square_{2.7}]$	25
I as a non-metal in the framework		$I_8[Sn_{10}Ga_{14}As_{22}]$	75
$I_8[Ge_{43.33}I_{2.67}]$	24	$I_8[Sn_{17}Zn_7As_{22}]$	75
$I_8[Si_{44.5}I_{1.5}]$[a]	27, 30	$I_8[Sn_{19.3}Cu_{4.7}As_{22}]$	31
		$I_8[Sn_{17.6}Cu_{6.4}As_{22}]$	31

[a] A compound with a framework of Si atoms.

group *Pm*3*n*, in which the 16*i* position is occupied simultaneously by geranium and arsenic atoms, was described only for the $I_8[Ge_{38}As_8]$ phase in paper [23] published in 1982. However, the reliability of these data was not discussed in the cited study.

As can be seen from Table 2, there is a series of compounds of the general formula $A_8[E_{38}M_8]$ (A = Na, K, Rb, Cs, Ba; E = Si, Ge, Sn; M = Al, Ga, In, Zn, Cd), whose structures are also characterised by mixed occupancies of the positions of the framework by atoms of different types. However, the latter crystallise in the centrosymmetrical space group *Pm* 3*n*. It should be noted that the distribution of the heterometal atoms M over the positions of the framework in these compounds differs from that observed in pnicogen-containing clathrates in that the 'heteroatoms' either occupy predominantly the 6*c* position or are statistically distributed over all three positions, as exemplified by the $[Ge_{38}Ga_8]$ frameworks. In this case, the loss of an inversion centre cannot lead to additional ordering of the structure. Besides, the difference in the chemical nature of the atoms occupying the same position in the compounds under consideration is less significant than that in the case of the germanium/pnicogen pair.

The guest atoms in the type-I clathrate structure occupy the 2*a* and 6*d* positions, *viz*., the centres of the pentagonal dodecahedra and tetrakaidecahedra, respectively. According to the results of X-ray and neutron diffraction studies, the guest atoms show very large displacement parameters because of the absence of 'rigid' bonds between the framework and the guest. As expected, atoms execute larger-amplitude thermal motions in a larger space. For some compounds, it was proposed [9, 34, 76 – 79] that the guest atoms should be displaced from the 6*d* position to a position with a higher multiplicity and partial occupancy, *viz*., to 24*k* or 24*j* with 25% occupancy each or to 12*h* with 50% occupancy (Fig. 3 *b*). As can be seen from Fig. 3, the 6*d* position is tetrahedrally coordinated by the 24*k* positions, the 24*j* positions form a square about the *6d* position, and the 12*h* positions linearly coordinate the 6*d* position. However, this model of arrangement of the guest atoms in large polyhedra is possible only for a limited number of structures. In most cases, this model is incorrect because no displacements of the guest atoms from the 6*d* position were revealed in low-temperature X-ray diffraction experiments.[32, 80]

There are two modes of formation of a superstructure based on the crystal structures of type I clathrates (Fig. 4). One mode is observed in the $I_8[Sn_{14}In_{10}P_{21.2}\square_{0.8}]$ compound,[29] which crystallises in the tetragonal system in the space group $P4_2/m$. In this structure, the unit cell volume increases by a factor of five compared to the unit cell volume of the starting clathrate ($a_{super} \approx \sqrt{5}a_{clath}$, $b_{super} \approx \sqrt{5}b_{clath}$, $c_{super} \approx c_{clath}$), which is accompanied by partial ordering of vacancies in the clathrate framework. Ordering insures against mixed occupancy of the same position simultaneously by three- and four-coordinate metal atoms.

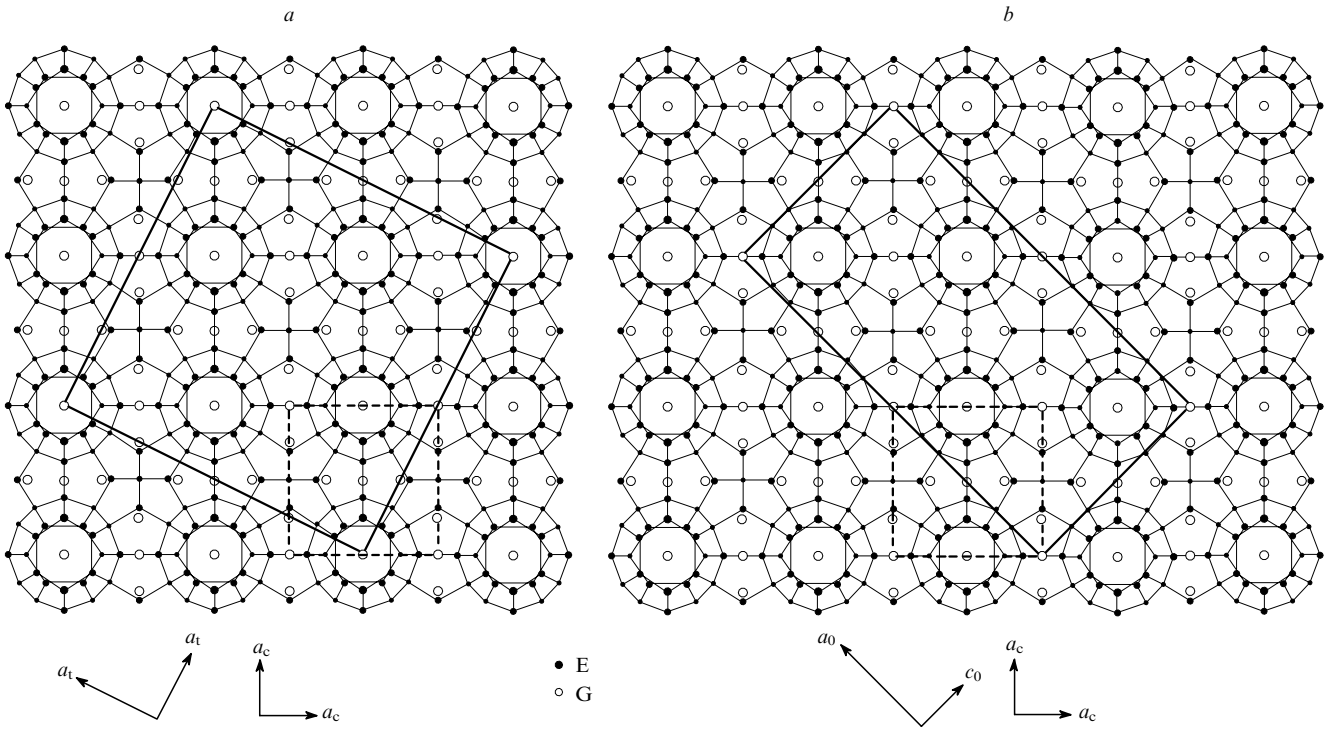


Figure 4. Superstructures of type I clathrates.
(*a*) The tetragonal superstruture $I_8[Sn_{14}In_{10}P_{21.2}\square_{0.8}]$, (*b*) the orthorhombic superstructure $Ba_8[Cu_{16}P_{30}]$; the initial cubic unit cell is indicated by dashed lines.

Another mode of formation of a superstructure is exemplified by the $Ba_8[Cu_{16}P_{30}]$ compound.[74] The latter is the only example of semiconducting clathrates, whose framework has no Group 14 elements. It crystallises in the orthorhombic system in the space group *Pbcn*, which is accompanied by an increase in the volume of the starting cubic unit cell by a factor of four ($a_{super} \approx \sqrt{2}a_{clath}$, $b_{super} \approx a_{clath}$, $c_{super} \approx 2\sqrt{2}a_{clath}$). In this compound, the copper atoms are always coordinated by four phosphorus atoms, whereas the phosphorus atoms have different coordination environments described as 3Cu + 1P, 2Cu + 2P and 1Cu + 3P. Evidently, this coordination of the copper atoms in the absence of a superstructure in the space group *Pm3n* can occur only if two positions are occupied by both the copper and phosphorus atoms.

Therefore, the formation of superstructures is, apparently, dictated by preferential coordination of atoms of different nature involved in the framework. Presumably, superstructures based on type I clathrates also occur in a number of other compounds (which prevents mixed occupancy of a position by atoms of different types). However, these types of ordering require a very large increase in the unit cell volume and, hence, may remain undetectable by conventional X-ray diffraction techniques.

2. Type II clathrate

The type-II clathrate structure also contains two types of polyhedra: pentagonal dodecahedra [5^{12}] and larger 16-face hexakaidecahedra [$5^{12}6^4$] (see Table 1). The type-I clathrate structure differs from the type-II clathrate structure (Fig. 5) in that the pentagonal dodecahedra in the former are not linked to each other, whereas these dodecahedra in the latter share faces and are packed in layers alternating in the order [ABC], which is typical of cubic close packing. The layers of pentagonal dodecahedra are linked to form a three-dimensional framework through hexakaidecahedra. The latter also share hexagonal faces and have a diamond-like arrangement in the cubic structure. The unit cell contains 136 atoms of the framework including 16 small and 8 large cavities. The formula of the corresponding ideal clathrate is $G^I_{16}G^{II}_8[E_{136}]$. As mentioned above, about 10 compounds have the type-II clathrate structure. This can be attributable to a large difference in the size of the polyhedra involved in the clathrate. As can be seen from Table 4, the type-II clathrate structure occurs either when compounds contain two cations, which differ substantially in size (for example, Na and Cs in $Na_{16}Cs_8[Ge_{136}]$) or when the guest atoms of one type occupy predominantly only one type of polyhedral cavity, whereas another type of cavity remains vacant. The type of the cavity being occupied depends on the size of the framework-forming element. In the case of tin, the large barium cations occupy only smaller cavities ($Ba_{16}\square_8[Ga_{32}Sn_{104}]$), whereas even rather small sodium cations occupy predominantly larger cavities in the framework formed by silicon atoms ($Na_x\square_{24-x}[Si_{136}]$, $x < 8$).

All compounds with the type-II clathrate structure crystallise in the cubic system in the centrosymmetrical space group *Fd3m*; 136 atoms of the framework occupy three positions, *viz.*, 8*a*, 32*e*

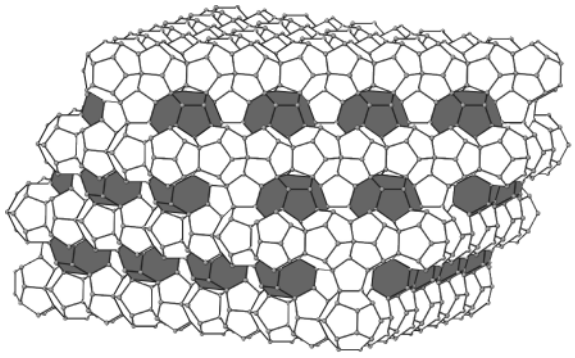


Figure 5. Overall view of the type-II clathrate structure.

Table 4. Compositions and structural features of polyanionic type-II clathrate phases.

Phase	Characteristics of the crystal structure	Ref.
$Na_x\square_{24-x}[Si_{136}]$	$1 < x < 23$; if $x < 8$, Na atoms occupy only larger cavities; at $x > 8$, smaller cavities begin to be filled	3, 40, 41, 81
$Na_x\square_{24-x}[Ge_{136}]$	$4 < x < 23$; if $x < 8$, Na atoms occupy only larger cavities; at $x > 8$, smaller cavities begin to be filled	82
$Cs_7\square_{17}[Si_{136}]$	Cs atoms occupy larger cavities	82
$Rb_8Na_{16}[Si_{136}]$	Rb atoms completely occupy larger cavities, Na atoms completely occupy smaller cavities	8
$Cs_8Na_{16}[Si_{136}]$	Cs atoms completely occupy larger cavities, Na atoms completely occupy smaller cavities	8, 83
$Rb_8Na_{16}[Ge_{136}]$	Rb atoms completely occupy larger cavities, Na atoms completely occupy smaller cavities	8
$Cs_8Na_{16}[Ge_{136}]$	Cs atoms completely occupy larger cavities, Na atoms completely occupy smaller cavities	8, 83
$Ba_{16}\square_8[Ga_{32}Sn_{104}]$	Ba atoms occupy only smaller cavities, and larger cavities are vacant	47, 84, 85

and 96*g*; 24 guest atoms occupy the 8*b* and 16*c* positions in the centres of the hexakaidecahedra and pentagonal dodecahedra, respectively. All positions of the framework in the type-II clathrate compounds (except for the $Ba_{16}\square_8[Ga_{32}Sn_{104}]$ compound) are occupied by atoms of one element. In the $Ba_{16}\square_8[Ga_{32}Sn_{104}]$ structure, the gallium and tin atoms are statistically distributed over all positions of the framework. Type II clathrates are characterised by full occupancies of the positions of the framework, whereas vacancies (if they are present) occur only in the guest positions (see Table 4).

3. Type III clathrate

Only two semiconducting clathrates with the type-III clathrate structure, *viz*., $Cs_{30}[Na_{2.5}Sn_{162.6}]$ and $Cs_{13.8}Rb_{16.2}[Na_{2.8}Sn_{162.3}]$, are known.[37] The structures of bromine hydrate $(Br_2)_{20}\square_{10}[(H_2O)_{172}]$ and dimethyl ether hydrate $(CH_3OCH_3)_{20}\square_{10}[(H_2O)_{172}]$ can be considered as prototypes of the type-III clathrate structure,[3] which consist of three types of polyhedra, *viz*., pentagonal dodecahedra $[5^{12}]$, larger tetrakaidecahedra $[5^{12}6^2]$ and even larger 15-face pentakaidecahedra $[5^{12}6^3]$ (see Table 1). Their ratio in the structure is 10 : 16 : 4, *i.e*., there are 30 polyhedra per unit cell. These polyhedra share faces to form a three-dimensional framework (Fig. 6) containing 172 atoms. The formula of the ideal type III clathrate is $G^{I}_{10}G^{II}_{16}G^{III}_{4}[E_{172}]$. Both compounds with the semiconducting type-III clathrate structure crystallise in the tetragonal system in the centrosymmetrical space group $P4_2/mnm$. All three types of cavities are completely occupied. In the $Cs_{30}[Na_{2.5}Sn_{162.6}]$ structure, all cavities are filled with cesium atoms. In the case of $Cs_{13.8}Rb_{16.2}[Na_{2.8}Sn_{162.3}]$, a situation, though more complicated, is also reasonable. In this structure, the largest pentakaidecahedra are occupied predominantly by cesium atoms, the smallest pentagonal dodecahedra are occupied predominantly by rubidium atoms, and the medium-sized tetrakaidecahedra are filled with cesium and rubidium atoms with equal probability.

The compositions of semiconducting type III clathrates differ slightly from the ideal composition, which is associated with the presence of vacancies in the framework. The reasons for the appearance of such vacancies and their amounts are discussed in detail below. The defect formation in the type-III clathrate structure differs from that in the type-I clathrate structure. In the type-III clathrate structure, vacancies are partially clusterised, *i.e*., a pair of tin atoms (Sn_2) is replaced by one sodium cation, which is located at the midpoint of the tin–tin bond (see Fig. 6). Hence, the formulas of the compounds under consideration can be written as $Cs_{30}[Na_{1.33x-10}Sn_{172-x}]$ and $Cs_{13.8}Rb_{16.2}.[Na_{1.33x-10}Sn_{172-x}]$ ($x \approx 9.6$).

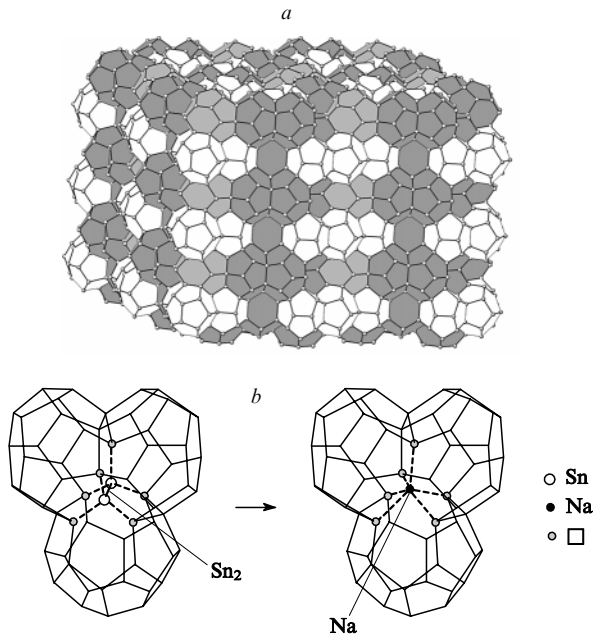


Figure 6. Type-III clathrate structure.
(*a*) Overall view, (*b*) formation of vacancies in the positions of tin atoms and replacement of these atoms with sodium atoms.

4. Type VIII clathrate

There are only two compounds, *viz*., α-$Eu_8[Ga_{16}Ge_{30}]$ (see Ref. 34) and α-$Ba_8[Ga_{16}\ Sn_{30}]$, with the type-VIII clathrate structure.[33,35] Both these compounds have a high-temperature β modification with the same composition and the type-I clathrate structure.[63] The type-VIII clathrate structure, unlike the type-I clathrate structure, has only one type of filled cavity (Fig. 7). These cavities can be described as distorted E_{20+3} polyhedra, which are derived from pentagonal dodecahedra as a result of the cleavage of three E–E bonds and the formation of nine new such bonds upon the addition of three additional E atoms. Since it is impossible to fill the complete space with this type of polyhedra, the structure also contains small eight-vertex cavities, which remain vacant. The formula of the ideal compound with the type-VIII clathrate structure is $G_8[E_{46}]$. Both known compounds crystallise in the cubic system in the non-centrosymmetrical space group $I\bar{4}3m$. The framework has 4 positions occupied by the E atoms of the framework (12*d*, 2*a*, 24*g* and 8*c*) and one guest position (8*c*). In both compounds, the gallium atoms are statistically mixed with Group 14 elements in all four positions of the framework. In studies,[34,35] the Ga : E ratio in the phases under consideration was demonstrated to be other than 16 : 30, *i.e*., these phases possess a certain homogeneity region and can contain a small excess of gallium. For the compound with E = Sn, this fact was established by X-ray diffraction.[35] In the case of E = Ge, non-stoichiometry was determined only on the basis of indirect evidence taking into account the physical properties of samples containing Ga and Ge in different ratios.[34]

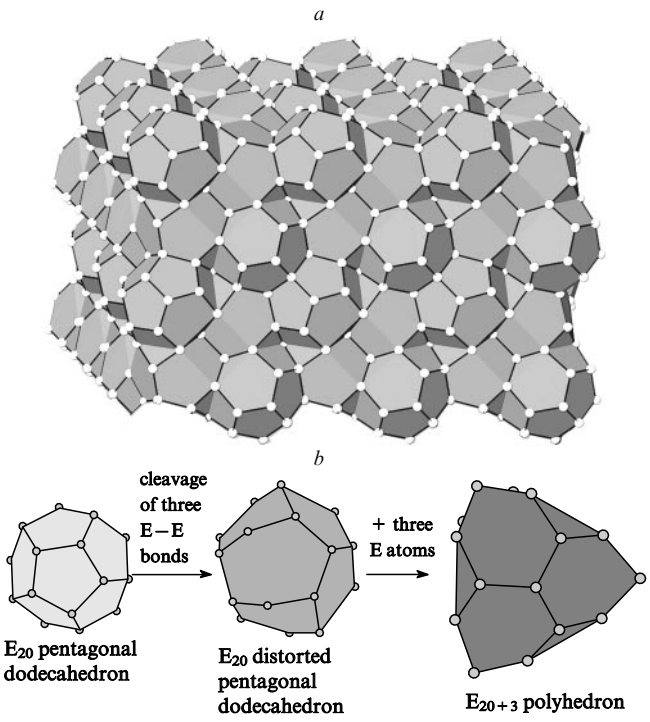


Figure 7. Type-VIII clathrate structure.
(*a*) Overall view, (*b*) scheme of distortions of the pentagonal dodecahedron.

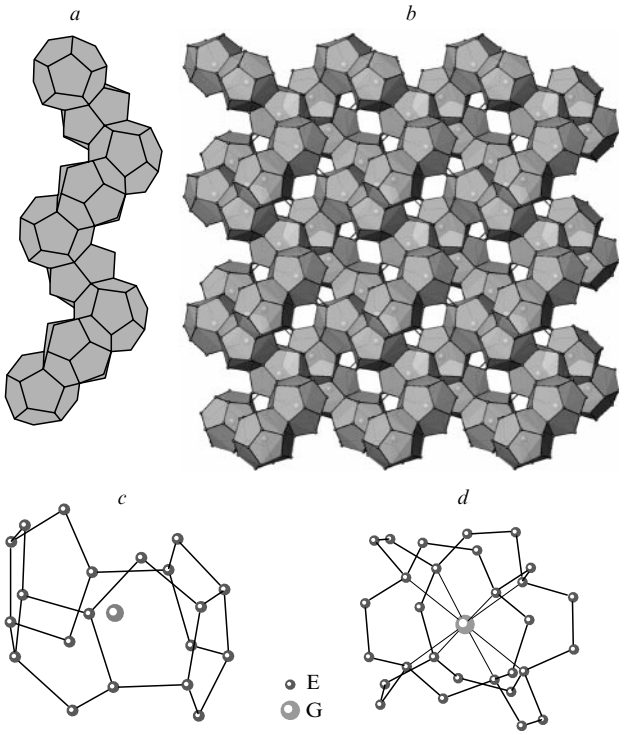


Figure 8. Type-IX clathrate structure.
(*a*) A chiral chain consisting of pentagonal dodecahedra, (*b*) a polyhedral representation of the structure, (*c*) the guest atom G^{II} in the open 20-vertex polyhedron, (*d*) the environment of the guest atom G^{III}.

5. Type IX clathrate

Type-IX clathrate compounds (or 'chiral' clathrates) crystallise in the cubic system in the non-centrosymmetrical space group $P4_132$. Eleven known compounds of this type are listed in Table 5. The main framework-forming polyhedron in the type-IX clathrate structure, like that in other clathrate structures, is a pentagonal dodecahedron. These polyhedra share faces to form a helix about each 4_1 axis (which accounts for the name 'chiral clathrate') (Fig. 8). The helical chains fill the space only partially, the channels between these chains being occupied by additional guest atoms of two types. The coordination of these atoms can be described as follows: one of these atoms is located in the 20-vertex open cavity and another atom is located in a distorted cube formed by the E atoms (see Fig. 8). The guest atoms located inside the pentagonal dodecahedra occupy the 8*c* position. Two other types of guest atoms can be described in different ways:

(1) both atoms completely occupy the 12*d* and 4*b* positions in the centres of the open twenty-vertex polyhedra and the cubes, respectively;[86–91, 94]

Table 5. Type-IX clathrate phases.

Framework-forming element	Phase	Ref.
Si	$Ba_6[Si_{25}]$	86
Ge	$Ba_6[Ge_{24}\square_1]$	87
	$Ba_{24}[Ge_{100}] \equiv Ba_6[Ge_{25}]$	88, 89
	$Na_2Ba_4[Ge_{25}]$	90
	$Ba_6[Ge_{23}Sn_2]$	87
	$Ba_6[Ge_{22}In_3]$	87
	$Ba_6[Ge_{21}In_4]$	36, 91
Sn	$K_6[Sn_{25}]$	92, 93
	$K_{7.4}[Sn_{25}]$	69
	$Rb_3Na_5[Sn_{25}]$	94
	$K_6[Sn_{23}Bi_2]$	92, 93

(2) the atoms in the centres of the open twenty-vertex polyhedra partially occupy the 24*e* position, and the atoms in the centres of distorted cubes completely occupy the 4*b* position;[69, 87, 92, 94, 95]

(3) both atoms partially occupy the 24*e* positions in the vicinity of the corresponding 12*d* and 4*b* positions.[93, 96]

It should be noted that the guest atoms in all models show large displacement parameters. In a number of studies (see, for example, Ref. 97), it was noted that a decrease in the temperature causes a phase transition accompanied by a change in the structure such that the atom is shifted from the 12*d* position to the 24*e* position with 50% occupancy.

The atoms of the framework occupy six positions, *viz*., three 24*e*, one 12*d* and two 8*c*. The type-IX clathrate structure differs essentially from all other types in that only 68 atoms of the framework (in two 24*e* positions and in the 12*d* and 8*c* positions) are four-coordinate, whereas 32 atoms (in the 24*e* and 8*c* positions) are three-coordinate. It should be noted that the type-IX clathrate structure has four formula units. The compositions of the clathrate phases given in Table 5 correspond to the compositions reported in the original studies. It can be seen that such compounds contain different amounts of guest atoms. This fact correlates with the electronic structures of semiconducting clathrates and is discussed in detail below.

6. Compounds structurally related to clathrates

Several compounds related to clathrates were described in the literature. The crystal structures of these compounds also contain the major polyhedron of clathrate structures, *viz*., the pentagonal dodecahedron. Examples are $Cs_3Na_{10}Sn_{23}$,[94] $Cs_2BaCu_8Te_{10}$,[98, 99] $Ba_{16}Na_{204}Sn_{310}$ (see Ref. 100) and $Te_{7+x}Si_{20-x}$ ($x \approx 2.5$).[101] The structure of the $Cs_3Na_{10}Sn_{23}$ compound contains layers of the face-sharing pentagonal dodecahedra $Cs@Sn_{20}$. These layers are analogous to the layers present in the type-II clathrate structure (see Fig. 5). In the $Cs_3Na_{10}Sn_{23}$ structure, these layers alternate with layers consisting of the $(Sn_4)^{4-}$ isolated tetrahedra, and the

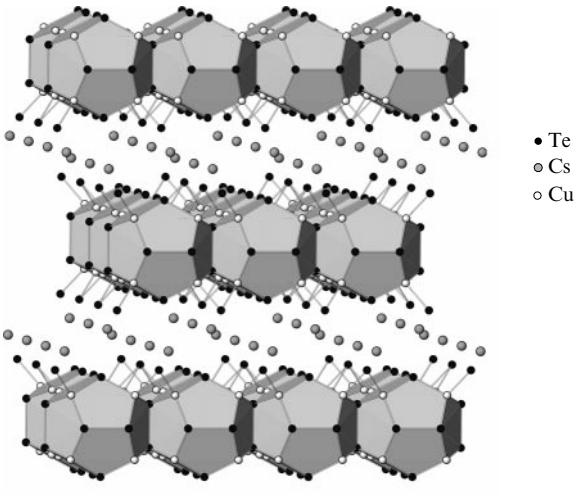


Figure 9. Crystal structure of $Cs_2BaCu_8Te_{10}$.

cavities between the polyhedra are occupied by sodium atoms. Another type of layer formed by the pentagonal dodecahedra is observed in the $Cs_2BaCu_8Te_{10}$ structure, in which the $Ba@Cu_8Te_{12}$ polyhedra share edges to form a layer. The layers are separated by cesium atoms (Fig. 9). The above-described compounds contain two-dimensional infinite fragments of clathrate structures.

The structures of the following two compounds have finite fragments. The structure of the $Ba_{16}Na_{204}Sn_{310}$ phase contains fragments of four vertex-sharing pentagonal dodecahedra $Ba@Sn_{20}$. Two other polyhedra of the host in this phase are the disordered $Na@Sn_{12}$ icosahedron and the 'empty' eight-vertex polyhedron Sn_8. The latter can be described as either a distorted cube or a distorted Archimedean antiprism. The space between the polyhedra is filled with sodium atoms. The structure of the $Te_{7+x}Si_{20-x}$ phase has the isolated pentagonal dodecahedra $Te@Te_{2.5}Si_{17.5}$, and the cavities between the latter are occupied by tellurium atoms. Interestingly, this compound is characterised by charge inversion, *viz*., the tellurium atoms, which are not involved in the polyhedron, bear a negative charge, *i.e*., they can formally be considered as Te^{2-} dianions.

A series of gallides and germanides of alkali, alkaline-earth and rare-earth metals, in which the positively charged guest metal atoms have rather high coordination numbers (from 14 to 19), were described in the literature.[102–115] Some researchers assigned these compounds to clathrate-like substances. However, in our opinion, it is unjustified to consider these compounds as related to clathrates because their crystal structures have no closed cavities and fragments of clathrate structures.

III. Electronic structures and properties of semiconducting clathrates

The electronic structures of semiconducting clathrates can qualitatively be described using the Zintl concept, *viz*.,the electron transfer from electropositive guest metal atoms to the framework formed by main-group atoms with localised covalent bonds.[38] Zintl phases are characterised by the strict correspondence between the crystal structure and electronic structures.

Classical Zintl phases are binary and ternary compounds, which contain alkali and alkaline-earth metals as cations and main-group elements from Groups 13–15 as anions and have structures of any complexity.[38] In such compounds, the cation donates electrons to the anion to form a closed-shell electronic configuration. The anion acquires an electron octet through the formation of two-centre two-electron homonuclear bonds and localised lone electron pairs. As a result, these compounds exhibit properties characteristic of Zintl phases. Evidently, if all atoms have closed-shell electronic configurations, all bonding and non-bonding (corresponding to lone electron pairs) states in the covalent anionic sublattice are filled, whereas all antibonding states are vacant. Correspondingly, Zintl phases exhibit semiconducting properties, even though they are polar intermetallides.

In addition to classical phases, there are the so-called metallic Zintl phases. These are compounds of Group 13 and 14 elements with alkali metals,[116] which can formally be described in terms of the Zintl concept. However, their properties differ from those predicted according to this concept. If the octet rule is obeyed, a change in the energy of interaction in going from a local level to an extended system can lead to the disappearance of a band gap and the appearance of metallic conductivity.[117,118] There are also 'non-traditional' Zintl phases. Among the latter are, for example, compounds containing transition metals, which cannot obey the octet rule but which can adopt the so-called closed-shell d-electron configurations (d^0, d^{10} and, sometimes, d^6 in an octahedral environment and d^8 in a square environment).[119,120] Inverted Zintl phases are generally assigned to 'non-traditional' phases. In such compounds, main-group elements form a cationic sublattice and acquire an electron octet, excess electrons being donated to eletronegative elements (halogens). This is accompanied by charge inversion: negatively charged halogen atoms are 'equivalent' to positively charged alkali and alkaline-earth metal cations in traditional Zintl phases.[38,121]

The detailed consideration of the Zintl concept and the properties of Zintl phases is beyond the scope of our review.‡ Here we demonstrate that most semiconducting clathrates are Zintl phases from the viewpoint of their formal electronic structures. However, some properties of these compounds cannot be explained in terms of the Zintl concept.

1. Type I clathrate

According to the Zintl concept, if the framework of the type I clathrate $A_8[E_{46}]$ is formed only by Group 14 atoms, which have four valence electrons and form four two-centre two-electron bonds, and has no vacancies, the $[E_{46}]$ framework should be electroneutral in the absence of guest atoms. The metal atoms A (alkali or alkaline-earth) placed in the polyhedral cavities in this framework acquire an electron octet due to donation of their valence electrons to the framework. A total of $8n$ electrons per formula unit (n is the valence of the A atom) are donated. Since these electrons occupy the antibonding conduction σ*-band of the host framework, the clathrate with the ideal composition $A_8[E_{46}]$ should exhibit metallic rather than semiconducting properties. Excess electrons in the σ*-band can be compensated in two different ways: by removal of some atoms of the framework or the partial replacement of the atoms of the framework by metal atoms having a smaller number of valence electrons.

In the former case, the removal of one E atom compensates four excess electrons. It is necessary to create $d = 8n/4$ vacancies in the framework. This situation is observed in alkali metal stannides ($d = 2$) of the general formula $A_8[Sn_{44}\square_2]$ (A = K, Rb, Cs) (see Table 2).[8,47,69,70]

In the case of heterovalent substitution, one heterometal atom M compensates $(14-z)$ excess electrons (z is the group number for the metal under consideration in the long-period form of the Periodic system of elements). The total number of metal atoms (y) required for the formation of the vacancy-free compound $A_8[M_yE_{46-y}]$ is calculated by the equation

$$y = \frac{8n}{14-z}.$$

The formulas of the ideal clathrates upon heterovalent substitution are given in Table 6.

Excess electron can also be compensated simultaneously through the formation of vacancies in the framework and hetero-

‡ These problems were discussed in detail in original studies.[38,121]

Table 6. Compositions with the type-I clathrate structure $A_8[M_yE_{46-y}]$, which were prepared by heterovalent substitution and obey the Zintl rule.

z	y	Composition ($n = 1$)	y	Composition ($n = 2$)
13	8	$A_8[M_8E_{38}]$	16	$A_8[M_{16}E_{30}]$
12	4	$A_8[M_4E_{42}]$	8	$A_8[M_8E_{38}]$
11	2.7	$A_8[M_{2.7}E_{43.3}]$	5.3	$A_8[M_{5.3}E_{40.7}]$
10	2	$A_8[M_2E_{44}]$	4	$A_8[M_4E_{42}]$

valent substitution. According to the Zintl concept, the coefficients y and d for the polyanionic clathrate $A_8[M_yE_{46-y-d}\square_d]$ are related by the equation

$$y(14-z) + 4d = 8n.$$

Such a 'twofold' compensation can be exemplified by the $Ba_8[Cd_4Ge_{40}\square_2]$ compound ($n = 2$, $z = 12$, $d = 2$, $y = 4$).[68]

In the case of heterovalent substitution of a p metal (Al, Ga, In, Zn or Gd) for a Group 14 element in polyanionic clathrates, the compositions determined by X-ray diffraction analysis are always identical to those predicted according to the Zintl concept (see Table 2). In some early studies, the synthesis of polyanionic clathrates, whose compositions do not satisfy the Zintl concept (for example, $K_8[Ga_{23}Sn_{23}]$ [122]), was mentioned. However, these data were not confirmed in later studies.[8, 46, 47, 55, 59] All clathrate compounds belonging to Zintl phases exhibit semiconducting and diamagnetic properties.[7, 9, 46, 47, 55–60, 68, 71, 72, 123]

Frameworks formed simultaneously by gallium and germanium atoms do not obey the Zintl principle. X-ray and neutron diffraction studies demonstrated that gallium atoms, unlike all other heteroatoms, are mixed with germanium atoms in all three positions of the clathrate frameworks.[8, 34, 57, 58, 62, 64, 65] Taking into account this fact, it can be hypothesised that the formation of phases, which exhibit metallic conductivity and whose compositions differ from those predicted in terms of the Zintl concept, is more favourable in mixed gallium-germanium systems.

Almost without exception, compounds prepared by heterovalent substitution of d metals for Group 14 elements do not satisfy the Zintl concept.[53] However, the compositions given in Table 2 were calculated on the assumption that all d-metal atoms are in the d^{10} state, although they can occur in other stable oxidation states. Besides, poor reliability factors ($R_1 \approx 6\%$–10%) may indicate that the structural features of the clathrate framework (for example, occupancies of atom positions) were not all established reliably.

The only europium-containing type I clathrate, *viz*., the β-$Eu_8[Ga_{16}Ge_{30}]$ phase,[34, 62, 124] is of particular interest. For this phase, the magnetic moment per europium atom is 7.9 μ_B, which corresponds to Eu^{2+}. Below 36 K, this phase behaves as a soft ferromagnetic material. At 36 K, ferromagnetic ordering (Fig. 10) occurs, which is accompanied by a stepwise change in the heat capacity.[34]

The compositions of binary clathrate silicides and the $Ba_8[Ge_{43}\square_3]$ compound deviate substantially from those predicted in terms of the Zintl principle. Recall that the Zintl concept is a simplified approach, according to which filling of electronic states can be considered on the basis of only formal oxidation states. Evidently, effects associated with the formation of energy bands in extended structures are ignored within the framework of this approach. The specificity of the electronic structures of clathrate silicides, which do not obey the Zintl rule, is apparently associated with the energy features of the atomic orbitals of silicon.[42, 82] The strength of the Si–Si bond (226 kJ mol^{-1}) [125] is substantially higher than that of the homoatomic bond between the germanium and tin atoms. Since the band gap in clathrates is small, the filling of the conduction band with excess electrons appears to be more favourable than the cleavage of the bonds between the silicon atoms and formation of vacancies in the clathrate framework. Consequently, there is no need for a strict

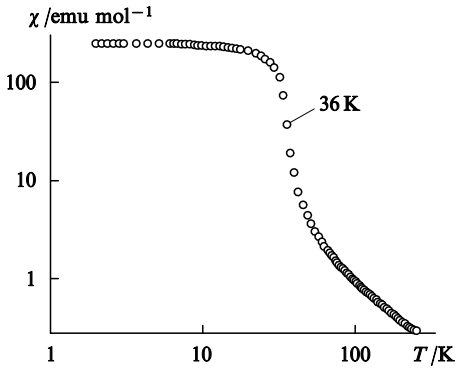


Figure 10. Temperature dependence of the magnetic susceptibility for β-$Eu_8[Ga_{16}Ge_{30}]$ according to the results of the study.[34]

correspondence between the composition of the compound and the number of electrons donated by the guest cation. Hence, many silicon-based clathrates have a wide non-stoichiometric region with respect to the cation. As an example we refer to $Rb_{8-x}Si_{46}$ ($x < 2$).[45] Such type I clathrates exhibit metallic conductivity and Pauli paramagnetism typical of metals.[126, 127]

In a series of studies, it was demonstrated that phases having no vacancies in the guest sublattice can be synthesised only under high pressure ($\sim$3 GPa).[48–51, 128] This method of synthesis allows one to prepare phases with unusual physical properties. Barium-containing silicides are low-temperature superconductors (T_c for $Ba_{7.76}\square_{0.24}[Si_{46}]$ is 9.0 K).[50, 51] This is the only example of superconductors with a framework formed by sp^3-hybridised silicon atoms. In studies,[50, 51] this fact was accounted for by partial overlapping of the s orbitals of the barium atoms with the orbitals of the atoms of the framework. An increase in the pressure leads to an increase in the amount of intercalated barium and an increase in the a parameter of the cubic unit cell. The partial replacement of barium with sodium or of silicon with germanium leads to a decrease in the superconducting transition temperature.[43, 44, 49]

The deviation of the composition of the germanium phase $Ba_8[Ge_{43}\square_3]$ (see Refs 49 and 61) from that predicted according to the Zintl concept ($Ba_8[Ge_{42}\square_4]$) is attributable to the fact that the formation of a large number of vacancies (four) in the framework is energetically less favourable than the formation of a smaller number of vacancies and doping of four excess electrons into the conduction band. Measurements of the resistive properties demonstrated that the $Ba_8[Ge_{43}\square_3]$ phase actually exhibits metallic conductivity.[61]

According to the Zintl concept, the framework of the inverse polycationic clathrates $X_8[E_{46}]$ (X is halogen) should donate eight excess electrons per formula unit to the X atoms. This is most easily achieved in the case of germanium compounds.[19–23] Each pnicogen atom in $X_8[Ge_{38}Z_8]$ (Z = P, As, Sb; X = Cl, Br, I) has 5 valence electrons, *i.e*., one electron more than the number of electrons required for the formation of four two-centre two-electron bonds. Correspondingly, 8 excess electrons are donated from eight pnicogen atoms to halogen atoms.

A different situation is observed in polycationic tin clathrates. The formula of ideal tin phosphide halide is $X_8[Sn_{24}P_{22}]$ (X = Br, I). Since each phosphorus atom donates one excess electron, while halogen atoms require only eight electrons to acquire an electron octet, the $X_8[Sn_{24}P_{22}]$ structure has $22-8 = 14$ excess electrons. These electrons can be compensated (as in the case of polyanionic clathrates) in two different ways: by the partial removal of the atoms of the framework or the partial replacement of the tin atoms with metal atoms having a smaller number of valence electrons.

In the former case, the removal of one phosphorus atom leads to compensation of five excess electrons. It is necessary to create $14/5 = 2.8$ vacancies. This corresponds to the $X_8[Sn_{24}P_{19.2}]$ com-

position, which is identical to that determined experimentally to within experimental error.[25, 31, 32]

In the case of heterovalent substitution, one heterometal atom M compensates $(14-z)$ excess electrons. To prepare the vacancy-free $X_8[M_ySn_{24-y}P_{22}]$ compound, the total number of metal atoms y can be calculated by the equation

$$y = \frac{14}{14-z}.$$

As can be seen from Table 3, the compositions of some vacancy-free tin phosphide halides, which were prepared by heterovalent substitution using p-metals (Ga, In, Zn, Gd) and even d-metals (Cu), are consistent with those predicted according to the Zintl concept.[26, 28, 29, 31, 75]

Excess electrons can be compensated simultaneously through the formation of vacancies in the framework and heterovalent substitution. In this case, according to the Zintl concept, the coefficients y and d for the polycationic clathrate $X_8[M_ySn_{24-y}P_{22-d}\square_d]$ are related by the equation

$$y(14-z) + 5d = 14.$$

The $I_8[Sn_{14}In_{10}P_{21.2}\square_{0.8}]$ ($z = 13$, $d = 0.8$, $y = 10$)[29] and $I_8[Sn_{20}Zn_4P_{20.8}\square_{1.2}]$ compounds ($z = 12$, $d = 1.2$, $y = 4$)[75] can serve as examples of the above-mentioned 'twofold' compensation.

The replacement of tin atoms with copper atoms in arsenide iodide can afford both a phase, which satisfies the Zintl principle ($I_8[Sn_{19.3}Cu_{4.7}As_{22}]$), and a phase containing an excess of copper ($I_8[Sn_{17.6}Cu_{6.4}As_{22}]$).[31] Since there are only a few tin arsenide iodides (see Table 3), the reasons for deviations from the Zintl principle remain unclear. There are two possible explanations: (1) the presence of transition metal atoms, which can adopt several stable electronic configurations; (2) as in the case of silicides, the cleavage of the As–As bonds and formation of vacancies are energetically less favourable than doping of excess electrons into the conduction band. A lack of data on the conductivity and magnetic susceptibility for these phases does not allow one to unambiguously decide between the above two schemes.

In the structures of all type I clathrates, vacancies are always located in the 6*c* position.[8, 25, 31, 32, 47, 49, 61, 64, 68–70] In this case, some atoms in the 24*k* position become three-coordinate. The presence of two types of tin atoms in the structures of alkali metal stannides was confirmed by ^{119}Sn NMR spectroscopy.[129] The distribution of the heterometal atoms over the positions of the framework in polyanionic clathrates differs from that observed in polycationic clathrates. In the former case, electropositive heterometals always fill first the 6*c* position and then the 16*i* position. The electronegative element (Sb) always fills the 24*k* position.[66, 67] Gallium, which is intermediate between the above-mentioned elements, can be mixed with Group 14 elements in all three positions of the framework.[8, 34, 57, 58, 62, 64, 65] In the case of polycationic clathrates, any heterometal occupies the 24*k* position together with tin,[26, 28, 29, 31, 75] which is accompanied by splitting of this position into two or three positions with partial occupancies, and some tin atoms are also three-coordinate. The coordination of tin atoms in polycationic clathrates can be confirmed not only by NMR spectroscopy but also by ^{119}Sn Mössbauer spectroscopy.[25, 26, 29, 75] In addition, the stereoactivity of the lone electron pairs on three-coordinate tin atoms can be judged from data on the quadrupole splitting of lines in the Mössbauer spectra.

The diamagnetic character of the temperature dependence of the magnetic susceptibility for certain polycationic type I clathrates, whose electronic structures obey the Zintl rule, is violated in the 200–250 K region, which is manifested in the appearance of a sharp jump in the curve $\chi(T)$.[32] As the field strength increases, this jump decreases up to its complete disappearance at $H \approx 5$ T. Low-temperature studies of the crystal structures of the $I_8[Sn_{24}P_{19.3}]$ and $Br_8[Sn_{24}P_{19.6}]$ compounds by X-ray diffraction analysis and Mössbauer, NMR, and X-ray photoelectron spectroscopy showed that a decrease in the temperature causes no structural changes.[32] Taking into account this fact, it can be concluded that a jump in the magnetic susceptibility curve is associated with either relaxation processes or a change in the mechanism of the electron–phonon interaction. Actually, the estimated value of the Debye temperature (below which, quantisation of thermal vibrations occurs) is 200–240 K. This conclusion is indirectly confirmed by the data on the temperature behaviour of the heat capacity of the $I_8[Sn_{24}P_{19.3}]$ phase. Thus, the maximum positive deviation from the Dulong–Petit law is observed at 250 K.[32]

An interesting and important transport property of semiconducting type I clathrates is their abnormally low heat conductivity.[7, 9, 34, 62, 72, 76, 78, 80, 123, 124, 130–132] At room temperature, the heat conductivity of many type I clathrates is 0.5–1.5 W m^{-1} K^{-1}, which is comparable to that of amorphous compounds. Moreover, a low-temperature region of the temperature dependence of the heat conductivity for most clathrates is typical of amorphous compounds (Fig. 11 *a*). This fact was initially explained by scattering of heat-carrying phonons by low-frequency vibrations of guest atoms inside the clathrate frameworks. Actually, calculations based on the Wiedemann–Franz law demonstrated that the electronic component of the heat conductivity is no higher than 6%–8%.[7, 9, 72, 78, 130] Consequently, the heat conductivity is determined primarily by its lattice component, and the guest atoms have high thermal parameters and can serve as efficient rattlers§ (Fig. 11 *b*). This mechanism is evidenced also by a slight decrease in the heat conductivity of most clathrates with decreasing temperature, which corresponds to a decrease in vibration amplitudes of the guest atoms.[80, 131] Such compounds are called phonon glasses, because glasses (in the general case, amorphous compounds) are characterised by a great number of structural irregularities, which effectively scatter pho-

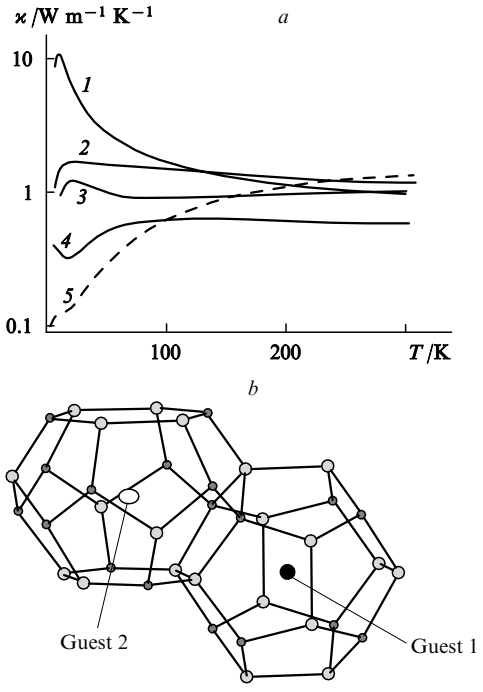


Figure 11. Temperature dependence of the heat conductivity for several type I clathrates (*a*) and anisotropic thermal displacements of the guest atoms in the clathrate polyhedra (*b*).
(*1*) $Cs_8[Sn_{44}\square_2]$, (*2*) $Rb_8[Zn_4Sn_{42}]$, (*3*) $I_8[Sn_{24}P_{19.3}\square_{2.7}]$, (*4*) β-$Eu_8[Ga_{16}Ge_{30}]$; data for vitreous silica (*5*) are given for comparison.

§ Weakly bound atoms or molecules, which can freely rotate or vibrate within a closed cavity and scatter heat-carrying phonons.

nons (the vibrational modes).[6] However, a detailed consideration of the temperature dependence of the heat conductivity showed that the region of this dependence below 50 K cannot be described as photon scattering by vibrations of guest atoms.[133] Two other possible mechanisms, *viz*., lattice relaxation and tunnelling of the guest atoms in a larger cavity to several nearby positions (see Fig. 3 *b*), were proposed.[34, 130, 133, 134] The characteristic features of a particular clathrate compound determine which process dominates.

The structures of the energy bands of type-I clathrate compounds were studied using various approximations, from the extended Hückel method to *ab initio* calculations.[9, 29, 38, 79, 135–144] Calculations showed that clathrates, which obey the Zintl rule, are narrow gap semiconductors. It appeared that the presence of vacancies predicted in terms of the Zintl concept is a necessary condition for the formation of semiconductors. If this condition is not met, one would expect the appearance of metallic properties.[29, 38, 141] For the polycationic clathrates, it was established that either orbitals of three-coordinate tin atoms having a lone electron pair or orbitals of heterometal atoms make the major contribution to the states in the vicinity of the Fermi level (Fig. 12).[29] The results of calculations for the $I_8[Sn_{24}P_{19.3}]$ phase agree well with the data from Mössbauer spectroscopy. The latter demonstrated that the lone electron pairs are not localised on tin atoms; instead, they form an extended band in the vicinity of the Fermi level.[29] Therefore, the properties of type I clathrates can be varied by changing the concentration of vacancies and performing various substitutions in the clathrate framework. Calculations also showed that the guest atoms in all type-I clathrate compounds are ionised.[29, 145] In particular, the charge on the halogen atoms in polycationic clathrates can be as high as -0.95, which is close to the corresponding oxidation state of the element. Arguments in favour of the atomic (non-ionised) state of the strontium atoms in $Sr_8[Ga_{16}\ Ge_{30}]$, which were adduced in several studies (see, for example, Ref. 77), were demolished in more recent studies.[144]

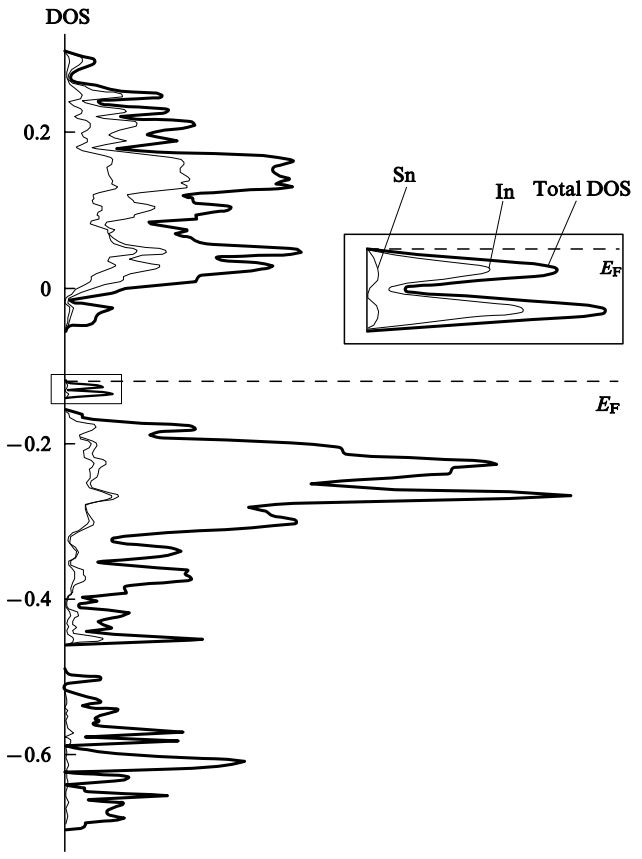


Figure 12. Plot of the density of states (DOS) for $I_8[Sn_{10}In_{14}P_{22}]$.[29]

2. Type II clathrate

In the framework of type-I clathrate compounds, as in the ideal type I clathrate, all atoms form four bonds. Correspondingly, all electrons donated by the guest atoms are excessive. Compensation of excess electron by replacing 32 tin atoms with gallium atoms occurs only in the $Ba_{16}\square_8[Ga_{32}Sn_{104}]$ compound (see Table 4).[47, 84, 85] This is sufficient for compensation of 32 electrons of 16 barium atoms. In all other cases, the compositions of the phases do not obey the Zintl rule. Such phases exhibit metallic conductivity and Pauli paramagnetism.[8, 83, 145, 146]

Studies of the band structures [126, 135, 146, 147] gave an insight into the electronic structures of type-II clathrate phases. Calculations for the hypothetical unfilled framework $[Si_{136}]$ showed that there is a strongly localised vacant nonbonding band with a capacity of 24 electrons in the vicinity of the Fermi level. The insertions of alkali metal (sodium) atoms into the polyhedral cavities in the framework of $Na_x[Si_{136}]$ is accompanied by ionisation of these atoms and filling of the nonbonding band with their valence electrons. If $x \geqslant 8$, the nonbonding band of the framework overlaps with the valence band. Hence, this compound must exhibit metallic properties. Correspondingly, at $x < 8$ silicide must possess semiconducting properties. However, the band gap between the valence and nonbonding bands is so narrow that it becomes smaller than kT at temperatures higher than 40 K, and $Na_x[Si_{136}]$ with $x < 8$ exhibits semiconducting properties only at low temperatures. Calculations of the band structures for silicides were confirmed by ^{29}Si and ^{23}Na NMR spectroscopy.[146, 147] The results of these calculations provide an explanation as to why the structure of the only barium-containing type II clathrate obeys the Zintl rule: the number of electrons donated by the barium atoms to the framework (32 electrons) is larger than the capacity of the nonbonding band (24 electrons), and doping of electrons into the conduction band is energetically unfavourable. That is why the type II clathrate, containing barium atoms as the guest, was synthesised only by partial heterovalent substitution of the atoms of the framework to compensate excess electrons.

It should be noted that silicon-based type II clathrates are characterised by very small compressibility comparable to that of silicon with a diamond-like structure.[148] Actually, the $Na_x[Si_{136}]$ compounds are not transformed into diamond-like silicon under high pressure; instead, they, like diamond-like silicon, are transformed into silicon with the structure of β-tin under a pressure of $\sim$11 GPa. The bulk modulum of $Na_x[Si_{136}]$ is only 8% smaller than that of diamond-like silicon. Hence, such clathrates hold considerable promise as superhard materials. Moreover, calculations demonstrated that carbon-based clathrates (if they will be synthesised) would be expected to have compressibility comparable to that of diamond and smaller than that of cubic boron nitride.[148, 149]

3. Type III clathrate

The general formula of type-III clathrate phases is $A_{30}[Na_{1.33x-10}Sn_{172-x}]$ ($x \approx 9.6$). The framework contains both isolated and 'clusterised' vacancies that formed upon the removal of a pair of bound tin atoms.[37] According to the Zintl concept, the presence of one isolated vacancy in the framework compensates four electrons. However, the removal of a pair of bound tin atoms compensates only six electrons. Actually, the removal of one tin atom gives rise to four three-coordinate tin atoms, each being involved in three bonds and having a lone electron pair. Five electrons are required for this coordination of the tin atom (three electrons for bonds with three other atoms and two electrons for the lone pair). Since the tin atom has only four electrons, one additional electron is necessary for each three-coordinate atom. Therefore, the removal of one tin atom compensates four electrons. The removal of a pair of tin atoms gives rise to only six three-coordinate atoms and, correspondingly, only six electrons are compensated (Fig. 13). It was demonstrated [37] that the ratio between the isolated and clusterised vacancies in the framework of type-III clathrate compounds, on the one hand, and the alkali

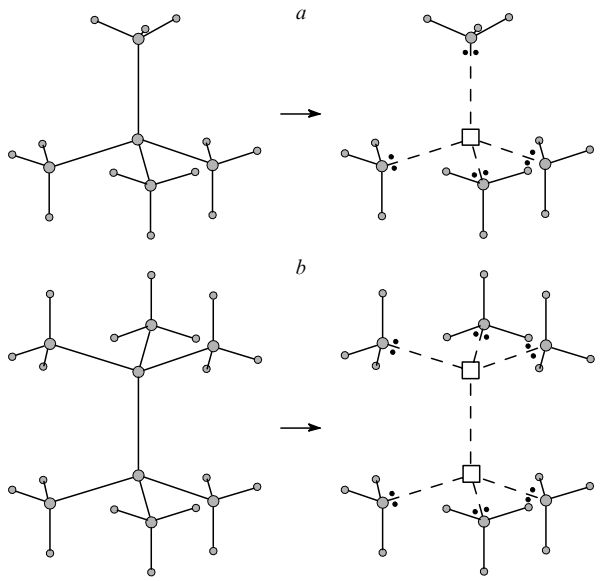


Figure 13. Clusterisation of the lone electron pairs of Group 14 elements in the case of formation of one (*a*) and two adjacent vacancies in the clathrate lattice (*b*).

metal atoms, on the other hand, is in complete agreement with the Zintl concept. Actually, magnetic measurements showed that both type-III clathrate compounds are diamagnetic.[37]

4. Type VIII clathrate

Type-VIII clathrate compounds are low-temperature polymorphs of type-I clathrate compounds.[63] The α phase (type VIII clathrate) of $Eu_8[Ga_{16}Ge_{30}]$[34] is stable up to 969 K, whereas the β phase (type I clathrate) is stable only over a narrow temperature range (969 – 972 K). At 972 K, the latter phase melts congruently. It should be noted that single-phase samples of the α and β phases were synthesised only using quenching to the corresponding temperatures (960 and 970 K for the α and β phases, respectively).

According to the Zintl concept, these compounds should have the same ideal composition: $A_8[Ga_{16}E_{30}]$ (A = Eu, Ba; E = Ge, Sn). However, the real compositions of these phases do not satisfy the Zintl rule. In early studies, the type-VIII clathrate compound in the Ba – Ga – Sn system was characterised as $Ba_8[Ga_{17.4}Sn_{28.8}]$.[33] More detailed investigation of the structure of this compound confirmed that its composition does not satisfy that predicted in terms of the Zintl concept. The refined composition of the phase is $Ba_8[Ga_{17.20(5)}Sn_{28.80(5)}]$.[35]

In the $Eu_8[Ga_{16}Ge_{30}]$ phase, as in other frameworks formed by gallium and germanium, the Ga : Ge ratio differs from 16 : 30.[133] The europium-containing α and β phases exhibit, on the whole, similar properties.[34] The magnetic moment per europium atom in the α modification also corresponds to Eu^{2+}. This phase is a soft ferromagnet and undergoes ferromagnetic ordering at 10.5 K. At this temperature, there is a jump in the temperature dependence of the heat capacity. A decrease in the temperature of ferromagnetic ordering compared to the analogous temperature for the type I clathrate is associated with the fact that the shortest Eu – Eu distances in the β phase are 5.23 Å, whereas the corresponding distances in the α phases are larger (5.56 Å).

5. Type IX clathrate

The type IX clathrate $A_6[E_{25}]$ is the only representative of clathrate compounds whose ideal framework contains three-coordinate atoms. Of the 25 atoms of the framework, 8 atoms are three-coordinate and 17 atoms are four-coordinate. Since each three-coordinate Group 14 atom requires one additional electron, the guest atoms should dope 8 electrons per formula unit into the framework to form an electroneutral compound. Among phases whose frameworks are formed exclusively by Group 14 atoms, the compositions of only two phases, *viz*., $Rb_3Na_5[Sn_{25}]$ (see Ref. 94) and $Ba_6[Ge_{24}\square_1]$,[87] obey the Zintl rule (see Table 5). In the latter phase, 4 excess electrons are compensated by the formation of one vacancy,[87] which is distributed over all positions of the framework in a complex fashion. It should be noted that the formation of this vacancy was not confirmed in other studies.[88, 89] By contrast, this phase was demonstrated to have no vacancies and its composition is inconsistent with the Zintl concept. Moreover, it was established[89] that it is impossible to synthesise a single-phase sample with composition $Ba_6[Ge_{24}\square]$.

Three phases, whose compositions obey the Zintl rule, *viz*., $Ba_6[Ge_{22}In_3]$,[87] $Ba_6[Ge_{21}In_4]$ (see Refs 36 and 91) and $K_6[Sn_{23}Bi_2]$,[92, 93] were synthesised by heterovalent substitution. In the first two phases, 4 excess electrons from the barium atoms are compensated by indium atoms (according to the Zintl concept, the four-coordinate indium atom compensates one electron, and the three-coordinated indium atom compensates two electrons). In the $Ba_6[Ge_{22}In_3]$ and $Ba_6[Ge_{21}In_4]$ phases, the indium atoms are distributed over all positions of the framework in a complex fashion. Hence, this distribution may also be considered as consistent with the Zintl concept. In the $K_6[Sn_{23}Bi_2]$ structure, the bismuth atoms occupy the three-coordinate positions of the framework. Each bismuth atom has 5 valence electrons, which are required for this coordination. Correspondingly, only 6 three-coordinate tin atoms remain in the framework, and six electrons from potassium atoms are sufficient for the formation of an electron-balanced compound. Phases whose electronic structures satisfy the Zintl rule, are diamagnetic narrow gap semiconductors.[36, 87, 91]

Compounds which do not obey the Zintl rule can be divided into two groups, *viz*., electron-excessive $Ba_6[Si_{25}]$ (+4*e*), $Ba_6[Ge_{25}]$ (+4e), $Ba_6[Ge_{23}Sn_2]$ (+4e) and $Na_2Ba_4[Ge_{25}]$ (+2e) and electron-deficient $K_6[Sn_{25}]$ (−2e).

The composition of potassium stannide with the type-IX clathrate structure has been initially characterised as $K_{7.4}[Sn_{25}]$.[69] However, the description of the positions and occupancies of the potassium atoms in this structure was doubtful, because the potassium atoms in this model were located at physically unreasonable short distances (2.92 Å). Later on, this phase was demonstrated to have a $K_6[Sn_{25}]$ composition.[92] To explain the fact that this composition does not satisfy the Zintl principle, the band structure of $K_6[Sn_{25}]^{2-}$ of the $K_6[Sn_{23}Bi_2]$ compound, which is isoelectronic to the Zintl phase, was calculated.[92, 93] This hypothetical structure is in complete agreement with the Zintl concept, and the calculations showed the typical semiconducting band structure with a band gap of ~1 eV. However, this band structure features an isolated filled band with a capacity of two electrons at the top of the valence band. Filling of this band influences primarily the interaction (repulsion) between 8 lone electron pairs of the tin atoms directed toward the centre of a distorted cube (see Fig. 8 *d*) and the potassium atom located in the centre of this cube. The repulsion is so high that a decrease in the number of electrons belonging to three-coordinate tin atoms is more favourable. Hence, the upper two-electron band in $K_6[Sn_{25}]$ is vacant. The replacement of two out of eight tin atoms with bismuth atoms (suppression of stereoactivity of the lone electron pair is more typical of the latter atoms) decreases repulsion between electrons giving rise to the classical Zintl phase $K_6[Sn_{23}Bi_2]$.[92, 93]

The band structures of electron-excessive phases were investigated.[95] In particular, the Fermi level was demonstrated to be located in the conduction band. According to the results of resistive measurements, such phases actually exhibit metallic conductivity.[86, 97, 150] The reason for the disorder in the guest sublattice (see the crystal structure of the type IX clathrate) was revealed. In the ordered structure, the Fermi level falls in a peak of the density of states. In the authors' opinion,[95] this fact may be indicative of the instability of the structure. Displacements of the

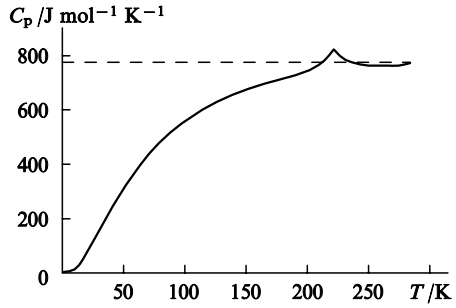


Figure 14. Temperature dependence of the heat capacity for $Ba_6[Ge_{25}]$.[97]

guest atoms from the ideal position to a partially occupied adjacent position leads to splitting of this peak into two peaks with larger and smaller energies. Therefore, a 'band' analogue of the Jahn–Teller effect is manifested in the crystal, and the density of states at the Fermi level substantially decreases.[95]

As expected, electron-excessive phases have metallic conductivity. A study of the heat capacity of the $Ba_6[Ge_{25}]$ phase revealed[97] a positive deviation from the Dulong–Petit law analogous to that observed for polycationic type I clathrates (Fig. 14). However, the authors of the cited study[97] explained this fact by a structural phase transition. At temperatures higher than the phase transition temperature, the barium atoms have high vibrations and can migrate from one partially occupied 24*e* position to another. A decrease in the temperature leads to 'freezing' of the barium atoms in the partially occupied 24*e* positions, which is indirectly confirmed by measurements of the temperature dependences of the electrical resistance, magnetic susceptibility and charge carrier mobility. In the $Na_2Ba_4[Ge_{25}]$ phase, 2/3 of barium atoms in the centres of the open 20-vertex polyhedra are replaced with sodium atoms. This phase is more ordered, and no structural transitions are observed in this phase down to 2 K.[97] Interestingly, both barium-containing germanides with the type-IX clathrate structure exhibit superconducting properties at low temperatures.[150] The superconducting transition temperatures T_c for the 'disordered' $Ba_6[Ge_{25}]$ phase and the 'ordered' $Na_2Ba_4[Ge_{25}]$ phase are 0.24 and 0.84 K, respectively. However, the temperature T_c of the disordered phase increases by a factor of more than 16 in response to external pressure (at 3.4 GPa, $T_c \approx 4.0$ K).[151] This fact was attributable to ordering of the barium atoms in the open cavities. Under high pressure, the barium atoms move from the partially occupied 24*e* positions to the 12*d* and 4*b* positions with 100% occupancy. The superconducting transition temperature for the ordered phase remains virtually unchanged under external pressure.[151] The above-mentioned compounds serve as examples of superconductors containing sp^3-hybridised atoms of p-elements.

IV. Methods for the synthesis of semiconducting clathrates

Since guest metal atoms (alkali metals, alkaline earth metals and europium) are highly reactive, polyanionic clathrates are generally synthesised under an inert gas (argon or helium) in sealed niobium or tantalum tubes, which are further placed in evacuated quartz tubes before annealing. Polycationic clathrates are more commonly synthesised simply in evacuated quartz tubes. It is more convenient to consider procedures for the synthesis of semiconducting clathrates for each particular main framework-forming element, *viz*., silicon, germanium or tin.

Silicon with a diamond-like structure has a very high melting point (1685 K) and, correspondingly, very low reactivity. Hence, the stoichiometric synthesis of binary clathrate silicides can be performed only at a high temperature under external pressure. For example, this procedure was used for the synthesis of $Ba_8[Si_{46}]$,[48–51] $Na_{8-x}Ba_x[Si_{46}]$,[43,44] $Ba_8[Si_{46-x-y}Ge_x\square_y]$ (see Ref. 49) and $Ba_{24}[Si_{100}]$.[86] The synthesis temperature was 1073–1573 K, and the pressure was 1.5–3 GPa. Another procedure for the synthesis involves thermal decomposition of binary silicides MSi (M = Na, K, Rb) to give $M_8[Si_{46}]$ or $M_x[Si_{136}]$ depending on the reaction conditions.[5,40,42,81,82] Heating to 500–700 K in the absence of dynamic vacuum can afford either type-I or type-II clathrate compounds with an x of ~ 10.[5,40–42] Under conditions of dynamic vacuum, syntheses produce primarily type II clathrate compounds. Depending on the reaction time, temperature and gas pressure, x can substantially be decreased (down to $x = 0.1$ at $\sim 10^{-3}$ Pa and 700 K).[152] Ternary clathrate silicides can be synthesised by the stoichiometric method. It should be noted that samples are usually pre-treated to enhance the reactivity of the starting compounds by performing either arc melting of the sample (for example, in the case of $Sr_8[Ga_xSi_{46-x}]$)[52] or heating of the sample to very high temperatures of 1300–1700 K (for example, in the case of $Ba_8[M_xSi_{46-x}]$, where M = Ni, Pd, Pt, Cu, Ag, Au),[53] generally, in an high-frequency furnace.

Germanium (T_m = 1210 K) is more reactive than silicon in spite of the fact that elemental germanium also has a diamond-like structure. Clathrate germanides can be synthesised by annealing stoichiometric amounts of the corresponding elements at 850–1250 K. As in the case of clathrate silicides, pre-treatment of samples is almost always required. For example, the $Ba_6[Ge_{25}]$ compound was prepared using arc melting[88] or induction heating.[89] The use of arc melting often leads to depletion of the reaction mixture due to evaporation of the most volatile metal and, correspondingly, to deviation from the starting stoichiometry. Because of this, this method is more often used for the synthesis of single crystals of clathrate compounds.[76,88] Single-phase samples are commonly synthesised using induction heating.[34,36,55–61,64,90,91] Since certain clathrate phases are stable only in a narrow temperature range (for example, β-$Eu_8[Ga_{16}Ge_{30}]$), the synthesis of such compounds involves quenching.[34]

Taking into account that the melting point of tin is low (505 K), stannides are generally prepared by annealing of a stoichiometric mixture of the elements without pre-treatment. In some instances, reaction mixtures containing an excess of tin are used. In such cases, tin serves also as a flux (for example, in the synthesis of the type IX clathrate $Rb_3Na_5[Sn_{25}]$).[91] The usual synthesis temperature is 600–700 K. Some tin-containing clathrates also cannot be prepared without quenching (for example, $Ba_8[Ga_{17.2}Sn_{28.8}]$).[33,35]

Polycationic clathrates are commonly synthesised by the simple stoichiometric method.[19–23,25,26,28,29,31,32] Elemental halogens are difficult to use because of their high volatility and also because chlorine and bromine are not solids under normal conditions. Therefore, halides of either metals or non-metals (MX_4, MX_2, TeI_4, ZX_3, where M = Ge, Sn; Z = P, As, Sb; X = Cl, Br, I) are usually used as the starting compounds. The synthesis temperatures vary from 670–830 K for tin-containing phases[25,26,28,29,31,32] to 1070 K for the $I_8[I_{1.5}Si_{44.5}]$ compound.[27,30] Polycationic clathrates can also be synthesised by the chemical transport reaction method. Since halogens and halides used as precursors are molecular compounds, they can serve as efficient transport agents. The chemical transport reaction method can be used for the preparation of single crystals and single-phase samples of polycationic clathrates. For example, single crystals of $Br_{2.4}I_{5.6}[Sn_{24}P_{19.2}\square_{2.8}]$ were grown in a temperature gradient of 825 – 725 K with the use of SnI_4 as the transport agent.[31,32]

V. Conclusion

Further studies of semiconducting clathrates will be aimed primarily at acquiring new fundamental knowledge and constructing new materials.

The fundamental scientific interest is associated primarily with the fact that particular type-I clathrate silicides [48, 50, 51] and type-IX clathrate germanides [150, 151] exhibit superconducting properties. Notwithstanding the fact that T_c for these compounds is no higher than 9.0 K, the occurrence of superconductivity in sp^3-hybridised systems is of obvious importance for a better understanding of this phenomenon. First data on the electron–phonon mechanism of superconductivity in clathrates were published as late as 2003.[153, 154]

An interesting field of investigation of semiconducting clathrates is concerned with elucidation of the reasons for the occurrence of such complicated structures, which are characterised by unusual filling of space with atoms and the unusual electron density distribution, and by the fact that the majority of these structures are thermodynamically stable and have diverse crystal structures. In particular, stability of the type-I clathrate compounds characterised by a distribution of the oppositely charged guest and host atoms was explained [155] in terms of periodic nodal surfaces (PNS),[155, 156] which allow one to relate the topology of the electron density distribution to the crystal structure. This method was also used for the description of the pathway of the phase transition between the α and β forms of $Eu_8[Ga_{16}Ge_{30}]$.[63]

Applied aspects of research on semiconducting clathrates are associated with the prospects of construction of new materials based on type-I clathrate compounds for thermoelectric cooling. The best currently available figure of merit (0.35) [157] is smaller than the maximum value (1.4) achieved for other types of inclusion compounds, *viz*., filled scutterudites.[132, 158] Nevertheless, there is no doubt that semiconducting clathrates hold promise,[11] and relative failures at the present stage of the investigation of these compounds are due to the fact that fundamental problems remain unsolved.[159, 160] Among such problems are the elucidation of the mechanisms of the abnormally low heat conductivity of clathrates and the prediction of fine changes in the electronic structure upon heterovalent substitution, including the prediction of the effective masses and concentrations of charge carriers.

Evidently, a combination of fundamental and applied studies [161] of semiconducting clathrates will contribute substantially to the development of inorganic and supramolecular chemistry, solid state chemistry and condensed matter physics.

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