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Ternary and quaternary chalcogenides of Group IB elements

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Abstract. Methods of synthesis, molecular and electronic structures and electrophysical, optical and magnetic properties of ternary and quaternary chalcogenides based on copper, silver and gold are considered. The possibility of the synthesis of chalcogenide analogues of high-temperature superconductors is discussed. The prospects of searching for new high-temperature superconductors in Ln – Cu – X systems, where Ln is a rare-earth element and X is S, Se or Te, are shown. The bibliography includes 148 references.

I. Introduction

The discovery of the high-temperature superconductivity in 1986 [1] has given powerful impetus to the development of solid-state chemistry. This has awakened great interest in metal oxide systems with the perovskite-like structures. High-temperature superconductors (HTSCs) with the superconducting transition temperatures (T_c) of up to 150 K (see Ref. 2) were synthesised (the data, while unconfirmed, on the synthesis of HTSCs with T_c of up to 250 K are also available in the literature [3, 4]). It has since become clear that the properties of new superconducting materials cannot be explained within the framework of the BCS theory (Bardeen – Cooper – Schrieffer). Apparently, the RVB (resonance valence bond) model proposed by Anderson [5] is most realistic.[5 – 9] This model assumes the occurrence of mixed-valence states in the system of chemically bonded atoms as an essential prerequisite for the high-temperature superconductivity. The mixed valence is necessary not only for the provision of the required carrier concentration and the equivalent positions for the carrier motion but also provides the basis for the coupling mechanism. In this connection, it becomes apparent that solid-state chemistry is of paramount importance in the solution of both theoretical and applied problems of physics of superconductivity.

In spite of the ten-year history of HTSCs, much in the chemistry of these materials remains unclear. Suffice it to mention that the problem associated with the estimation of the degree of oxidation of copper in metal-oxide samples, which is of importance for constructing the theory of HTSCs, is still debated. Leaving aside the details of this problem, let us mention a study,[10] in which the authors used X-ray emission spectroscopy for estimating the degree of oxidation of copper atoms in HTSCs. This method is free from the drawbacks of X-ray photoelectron spectroscopy (XPS), which is most often used for these purposes.

The role of oxygen atoms in HTSCs also remains unclear. In the available chemical models of superconductivity of HTSCs, which are based on Anderson's ideas,[11 – 13] the possibility of formation of weakly bound O_4 complexes upon transformation of HTSCs into the superconducting state is considered. The bond strength in these complexes is determined, on the one hand, by the sizes of the cations and, on the other hand, by the concentration of holes, which disturb the antiferromagnetic order in the initial dielectric system. Taking into account the greater ability of sulfur and selenium atoms to form polychalcogenide ions, chalcogenide analogues of HTSCs would be expected to possess stronger electrophysical characteristics compared to those of oxide HTSCs. This idea was proposed, for example, in the study;[14] simultaneously, it was assumed that the structural characteristics remain unchanged. The prospects for synthesising HTSCs based on thio-, seleno- and tellurocuprates are very attractive because chalcogenides of transition metals, in particular, copper chalcogenides, provide substantially greater possibilities for the preparation of compounds possessing various physicochemical properties compared to those of the corresponding oxides. The most essential differences consist in the higher covalence of the metal – chalcogen bonds, the ability of chalcogen atoms to form bonds with each other resulting in molecular anions and the higher ability of metal atoms to form metal – metal bonds (due to the lower formal charge). Owing to these facts, chalcogenides of Group IB metals can exhibit a broad spectrum of electrical (from dielectric to superconducting [15]) and magnetic properties (from diamagnetism to temperature-independent paramagnetism).

Table 1 gives the structural and electrophysical characteristics of selected superconductors based on chalcogenides of transition metals, *viz*., chalcogenides of copper and rare-earth elements, which are structural elements of HTSCs, as well on some ternary chalcogenides characterised by high *T*c values. Analysis of these data suggests that a search for HTSCs in M – Ln – X systems, where M is IB Group metal, Ln is a rare-earth element and X is chalcogen, may have promise. Thus, in the studies of the $Cu_2S - La_2S_3$ system performed in 1968 – 1972,[19 – 21] ternary sulfides, *viz*., the hexagonal $Cu_2La_4S_7$ and monoclinic $CuLaS_2$ phases, were detected. However, Andreev [22] studied the same system in 1988 and found only the $CuLaS_2$ phase. Later on, Andreev published the paper entitled 'The $Cu_2S - BaS$ system as a possible HTSC', [23] where he demonstrated that two phases, *viz*., the tetragonal $BaCu_2S_2$ and orthorhombic $BaCu_4S_3$ phases, exist

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Table 1. Structural and electrophysical characteristics of selected chalcogenide superconductors.[16–18]

Compound	T_c /K	Density of states /cm^{-3}	Lattice type	Composition
CuS	1.65	$\sim 10^{20}$	hexagonal	$Cu_4^+Cu_2^{2+}\cdot(S_2^{2-})_2(S^{2-})_2$
CuS_2	1.48–1.53	$\sim 10^{21}$	pyrite, cubic	$Cu^{2+}(S_2^{2-})$
$CuSe_2$	2.30–2.43	$\sim 10^{21}$	the same	$Cu^{2+}(Se_2^{2-})$
$CuTe_2$	1.25–1.3	$\sim 10^{21}$	"	$Cu^{2+}(Te_2^{2-})$
YS	1.9	$\sim 10^{22}$	NaCl, cubic	Y^{2+}/Y^{3+}
YSe	2.5	$\sim 10^{22}$	the same	Y^{2+}/Y^{3+}
YTe	2.05	$\sim 10^{22}$	"	Y^{2+}/Y^{3+}
LaS	0.87	$\sim 10^{22}$	"	La^{2+}/La^{3+}
LaSe	1.02	$\sim 10^{22}$	"	La^{2+}/La^{3+}
LaTe	1.48	$\sim 10^{22}$	"	La^{2+}/La^{3+}
La_2Se_3	1	semiconductor	cubic	La^{2+}/La^{3+}
La_3S_4	8–11.5	6×10^{21}	the same	La^{2+}/La^{3+}
La_3Se_4	7.63–9.4	10^{21}–10^{22}	"	La^{2+}/La^{3+}
La_3Te_4	4.61	–	–	–
$AgMo_4S_5$	8.9	–	–	–
$Cu_{1-1.9}Mo_3S_4$	10.9–10.5	–	–	–
$Li_xTi_{1.1}S_2$ ($0.1 < x < 0.3$)	10–13	–	hexagonal	Ti^{3+}/Ti^{4+}

in this system. In 1994, Chinese researchers[24] at the National Laboratory of Superconductivity synthesised a series of oxyselenides LnCuSeO (Ln = La, Sm, Gd or Y). The structures of the latter contain the alternating $[Ln_2O_2]$ and $[Cu_2Se_2]$ layers. Analogous layers have been found previously by Popovkin[25] in oxyselenide BiCuSeO. Attempts were undertaken to perform partial replacement of oxygen atoms in HTSCs by halogen or chalcogen atoms. These attempts often cast doubt from the chemical standpoint[14,26,27] and do not solve the problem because they allow only an insignificant amount of oxygen to be replaced by chalcogen. The effect of the latter in these systems can be considered only as a weak perturbation, which was in essence found in the above-mentioned studies.

As early as 1991, we attempted to synthesise chalcogenide analogues of HTSCs, in particular, $La_2CuS_{4+\delta}$ and $YBa_2Cu_3S_{6+\delta}$.[28] However, because of difficulties associated with the preparation of a single phase and the lack of data on simpler systems (for example, Ba–Cu–S and Cu–Ln–S), we turned our attention primarily to ternary systems consisting of chalcogenides of Group IB metals and chalcogenides of alkali, alkaline-earth or rare-earth metals.

Nevertheless, even regardless of the problem of HTSCs, the success achieved in the chemistry of ternary and quaternary chalcogenides based on Group IB elements within the last decade is so impressive that it makes sense to expose not only chemists and physicist involved in studies of HTSCs but also researchers working in other fields to the results obtained. The present review is devoted to analysis of methods of synthesis and molecular and electronic structures of chalcogenides in relation to their magnetic and electrophysical properties.

Molecular polychalcogenides are considered first because it is in this class of compounds that sulfides and selenides differ most sharply from the corresponding oxides. We next consider the coordination polymers based on polychalcogenides of Group IB metals. Finally chalcogenides containing only X^{2-} and/or X_2^{2-} ions, *i.e.*, the structural elements identical to those in oxide HTSCs, are considered. Tellurides are considered at the end of each chapter for two reasons. First, tellurium has peculiarities and the properties of tellurides differ from those of the corresponding sulfides and selenides and second, these compounds are poorly known.

II. Molecular copper, silver and gold polychalcogenides

Molecular polychalcogenides of Group IB metals containing isolated $[M_nX_m]^{q-}$ clusters (M = Cu, Ag or Au; X = S, Se or Te) were virtually unknown up to the early 1980s.[29] (The synthesis of polynuclear copper sulfide complexes was reported for the first time in 1983.)

The $(Et_4N)_3[Cu_3(S_6)_3]$ complex was prepared by the reaction of copper(II) acetate with an ethanolic solution of polysulfides.[30] The complex contains the complex $[Cu_3(S_6)_3]^{3-}$ ion in which the Cu^+ ions are chelated by the hexasulfide ions (Fig. 1). One of the terminal sulfur atoms of each S_6^{2-} ion acts as a bridge and is involved in formation of the central six-membered Cu_3S_3 ring. In the following year,[31] researchers succeeded in isolating salts, which contain $[Cu_3(S_4)_3]^{3-}$ ions and are structurally similar to $[Cu_3(S_6)_3]^{3-}$. In this study, the $(Ph_4P)_4[Cu_2S_{20}]$ salt containing the $[S_6CuS_8CuS_6]^{4-}$ ions in which two CuS_6 rings are bound to each other through the bridging S_8^{2-} anion was also described. Analogous silver salts containing the $[Ag_2S_{20}]^{4-}$ ions were also obtained.[32] Note that in all these salts, the copper and silver atoms adopt the coordination number of 3, which is rarely observed in the chemistry of coordination compounds.

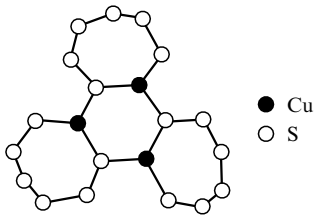


Figure 1. Structure of the $[Cu_3(S_6)_3]^{3-}$ anion.[29]

Müller and coworkers synthesised a series of four-nuclear clusters of the general formula $[Cu_4(S_4)_{3-x}(S_5)_x]^{2-}$. These clusters contain the tetrahedral Cu_4 core in which the copper atoms are chelated by the bridging S_4^{2-} and/or S_5^{2-} ions. All members of this series were isolated, *viz.*, salts with $x = 0$,[31] 1, 2[33] and 3.[34] The structure of the $[Cu_4S_4(S_5)_2]^{2-}$ cluster is shown in Fig. 2. It should be noted that these clusters provide rare examples of coexistence of the MS_4 and MS_5 chelates.

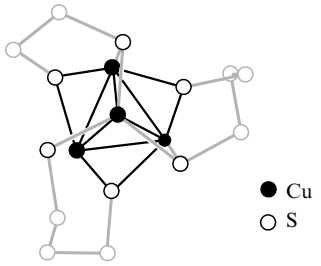


Figure 2. Structure of the $[Cu_4S_4(S_5)_2]^{2-}$ anion.[33]

In 1984, the $(Ph_4P)_2[Cu_6(S_4)_3S_5]$ salt was synthesised virtually simultaneously at the laboratories headed by Henkel[35] and Müller.[36] This salt can be prepared either by the reaction of $CuCl_2\cdot 2H_2O$ with a threefold excess of NaSR (R = Et or CH_2Ph) in methanol[35] or by the reaction of $Cu(acac)_2$ with an ethanolic solution of polysulfides.[36] In both cases, the salt was isolated as orange-red crystals upon addition of a solution of Ph_4PBr to the

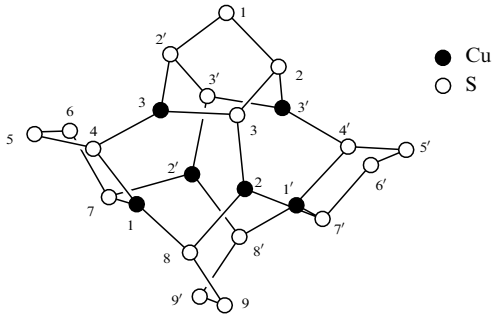


Figure 3. Structure of the $[Cu_6(S_4)_3S_5]^{2-}$ anion.[36]

reaction mixture. In this complex, a new coordination mode was found (Fig. 3). Six copper atoms form two distorted tetrahedra, whose vertices are occupied by the Cu(1), Cu(2), Cu(3), Cu(1′), Cu(2′) and Cu(3′) atoms. These tetrahedra are linked *via* the shared Cu(3)–Cu(3′) edge. The metal atom is coordinated by the tetrasulfide ions only through the terminal atoms, while the pentasulfide ions are coordinated to the metal atoms through four sulfur atoms [S(2), S(2′), S(3) and S(3′)].

In the laboratory headed by Henkel,[37] the $(Ph_4P)_4[Cu_{12}S_8]$ salt containing the $[Cu_{12}S_8]^{4-}$ cluster ions was synthesised. This salt was prepared as wine-red needles by the reaction of $CuCl_2 \cdot 2H_2O$ with a threefold excess of NaSEt in methanol (~ -78 °C) followed by addition of Li_2S and (after completion of the reaction) of a solution of Ph_4PBr. The $[Cu_{12}S_8]^{4-}$ anion has the ideal O_h symmetry. The sulfur atoms occupy the vertices of the cube and the copper atoms occupy the centres of the edges.

Later on, Marbach and Strähle [38] isolated an analogous gold complex as the tetraphenylarsonium $(Ph_4As)_4[Au_{12}S_8]$ salt. The $[Au_{12}S_8]^{4-}$ and $[Cu_{12}S_8]^{4-}$ anions have identical structures. In 1992, Kanatzidis and Huang [39] prepared the $(Et_4N)_3[NaAu_{12}Se_8]$ complex, which is the selenium analogue of the $(Ph_4As)_4[Au_{12}S_8]$ salt. The larger size of the selenium atom compared to that of the sulfur atom allows Na^+ ions to occupy the centres of the $[Au_{12}Se_8]^{4-}$ cuboctahedra. Hence, this complex is one of a few examples of inorganic cryptands. The Na^+ ion occupies the inversion centre. The distances from the sodium ion to the gold ions are shorter than those to the selenium atoms. Apparently, the interactions between the sodium ion and the twelve Au^+ ions are stronger. The authors [39] believed that this fact reflects the general tendency of the Au^+ ions to interact with alkali-metal ions. Note that the Au^+ or Cu^+ ions in the $[M_{12}X_8]^{4-}$ complexes (M = Au or Cu) have a typical linear coordination.

An example of a supposedly extremely large copper chalcogenide cluster was described in the study.[40] The authors succeeded not only in isolating the $[Cu_{146}Se_{73}(Ph_3P)_{30}]$ cluster but also in characterising it structurally. Although this compound is not a purely chalcogenide cluster because it contains the triphenylphosphine group, it corresponds to the subject of this review because this compound is formally a derivative of copper selenide $Cu_2Se-\{[Cu_2Se]_{73} \cdot 30(Ph_3P)\}$. This cluster is also of interest because it is a semiconductor with the conductivity $\sigma_{RT} = 1.5 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$. The selenium atoms in this cluster form three planar layers consisting of 21, 31 and 21 atoms (*ABA* packing) arranged in a close packed fashion. The copper atoms occupy the cavities in this packing. In the crystal, the clusters are arranged in such a way as to form cavities (channels) with a diameter of 1.6 nm. When crystallisation is performed from organic solvents, channels are occupied by the solvent molecules, which can be, however, removed under mild conditions without destruction of the crystal lattice. For example, 42 tetrahydrofuran molecules can add per formula unit of the cluster.

In the above-considered examples, the specificity of the Cu^+, Ag^+ and Au^+ ions is not manifested. Let us consider examples of chalcogenides, in which this specificity is apparent. The Au^+ ion, like the Cu^+ ion, forms a complex with the tetrasulfide ion with

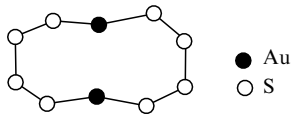
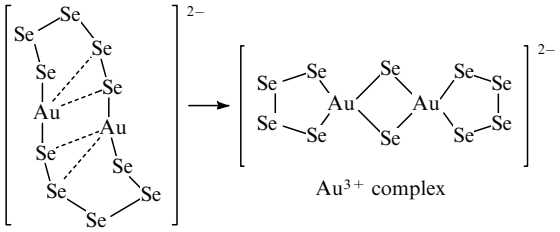


Figure 4. Structure of the $[Au_2(S_4)_2]^{2-}$ anion.[34]

composition $[Au_2(S_4)_2]^{2-}$.[34] Unlike analogous copper complexes, the gold(I) tetrasulfide complex can be described as a ten-membered ring, in which the Au^+ ion has a nearly linear coordination (Fig. 4).

The gold(I) pentaselenide complex was isolated as the $[(Ph_2P)_2NPh_2]_2[Au_2Se_{10}]$ salt. However, according to the data of X-ray diffraction analysis,[41] this complex is in fact an Au^{3+} derivative and contains coordinated selenide and tetraselenide ions. It was suggested that the Au^+ complex with the Se_5^{2-} ions in which the Au^+ ion has linear coordination, was actually formed at the initial stage. However, the subsequent intramolecular two-electron transfer from the Au^+ ion to the terminal Se–Se bond afforded the Au^{3+} and Se^{2-} ions and the Se_4^{2-} ions were formed from the Se_5^{2-} ions. The complex $[Se_4AuSe_2AuSe_4]^{2-}$ ion is planar, like the majority of Au(III) complexes.



Oxidation of Au(I) with the pentaselenide ion proceeded unusually. The reaction of $AuCl_3$ with Na_2Se_5 upon addition of a Ph_4PBr solution to the reaction mixture afforded gold and the product of oxidation of the pentaselenide ion, *viz.*, $(Ph_4P)_2Se_{11}$, *i.e.*, Au^{3+} was reduced with the pentaselenide ion. Apparently, the only analogous reaction is the reaction in the $Tl^+ - I_3^-$ system in which Tl^{3+} ions were completely reduced with I^- ions to Tl^+. However, Tl^+ ions reacted with an excess of I_3^- ions to form the Tl^{3+} complex with composition $[TlI_4]^-$.[41]

Polyselenide Au(I) complexes were prepared with the use of polyselenides Se_n^{2-} with $n = 1-4$.[42] Thus, the reaction of AuCN with a Na_2Se_2 or Na_2Se_3 solution in the presence of Ph_4PCl yielded the $(Ph_4P)_2[Au_2Se_2Se_3]$ salt containing the seven-membered cyclic $[Au_2Se_2Se_3]^{2-}$ anions (Fig. 5). The complex anion adopts an envelope conformation with the linear coordination of the Au^+ ions. The reaction performed under analogous conditions with the use of K_2Se_4 instead of Na_2Se_2 or Na_2Se_3 gave the $(Ph_4P)_2[Au_2Se_2Se_4]$ salt. This salt contains the eight-membered cyclic anion in which two Au^+ ions are symmetrically coordinated by the diselenide and tetraselenide ions.

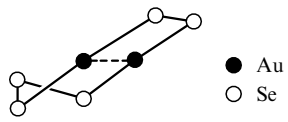


Figure 5. Structure of the $[Au_2Se_2Se_3]^{2-}$ anion.[42]

Finally, the reaction with the use of pentaselenide K_2Se_5 gave the $K_2[Au_2Se_2(Se_4)_2]$ complex. Unlike the two above-described complexes, the latter complex contains the Au^{3+} ion as a result of the higher oxidising capacity of the Se_5^{2-} ion compared to those of the Se_4^{2-} and Se_3^{2-} ions.[43]

$$2Se_5^{2-} + 2e \longrightarrow 2Se_4^{2-} + Se_2^{2-},$$

$$Au^{+} - 2e \longrightarrow Au^{3+}.$$

In addition to the above-mentioned $[Ag_2S_{20}]^{4-}$ anion, the Ag^+ complex with hexasulfide ions with composition $[Ag_2(S_6)_2]^{2-}$ is known. In this complex, the coordination of the S_6^{2-} ligands is analogous to that observed in the $[Cu_3(S_6)_3]^{3-}$ anion, with the only difference that the binuclear $[Ag_2(S_6)_2]^{2-}$ anion contains the four-membered Ag_2S_2 rings.[44]

The coordination of the tetraselenide anions by the Ag^+ cations is also very similar to that observed in Cu^+ salts. Thus, four-nuclear silver tetraselenides $(Et_4N)_4[Ag_4(Se_4)_4]$ and $(Pr_4N)_2[Ag_4(Se_4)_3]$ were isolated.[45] The $[Ag_4(Se_4)_4]^{4-}$ anion is formed by four Ag^+ ions, which occupy the vertices of the planar rhombus and which are linked *via* the bridging Se_4^{2-} ligands (Fig. 6). The silver atoms in this cluster are nonequivalent. The coordination environment about two of them [Ag(1) and Ag(1′), see. Fig. 6] is a tetrahedron, while two other atoms [Ag(2) and Ag(2′)] have a planar-trigonal coordination. Analogously, the Se_4^{2-} ions are also nonequivalent. Two of them link three silver ions each and the remaining two complex ions link two silver ions each.

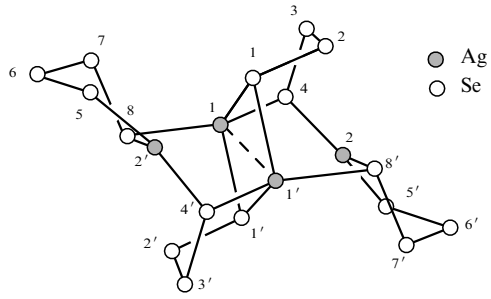


Figure 6. Structure of the $[Ag_4(Se_4)_4]^{4-}$ cluster.[45]

The structure of the cluster $[Ag_4(Se_4)_3]^{2-}$ ion (Fig. 7) is based on the tetrahedral cage formed by the Ag^+ ions, which are linked *via* three Se_4^{2-} ligands. This cage, in turn, forms the distorted adamantane-like central Ag_4Se_6 core in which all silver atoms adopt a planar-trigonal coordination.

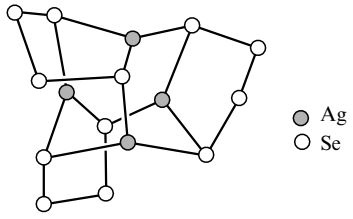


Figure 7. Structure of the $[Ag_4(Se_4)_3]^{2-}$ cluster.[45]

The complex copper and silver selenides, *viz.*, $[Cu_2Se_4(Se_5)_2]^{4-}$, $[Cu_4(Se_4)_{2.4}(Se_5)_{0.6}]^{2-}$ and $(Ph_4P)_2.[Ag_4(Se_4)_{3-x}(Se_5)_x]$, which are related to the above-described copper sulfides $[Cu_4(S_4)_{3-x}(S_5)_x]^{2-}$, were also described.[46,47] These salts were prepared by the reaction of CuCl with a melt of polyselenide Li_2Se_n or by fusing a mixture of $CuCl_2$, sodium and selenium. Their structures are similar to those of the corresponding sulfides.

The mononuclear complexes with the nonasulfide ion are known only for gold and silver. Marbach and Strähle isolated cyclic nonasulfidoaurate(I) $(Ph_4As)[AuS_9]$.[48] Its structure is shown in Fig. 8. The Au^+ ion binds the terminal sulfur atoms of the ligand and has a nearly linear coordination [the S(1)AuS(9) angle is 176°]. The analogous silver salt $(Ph_4P)[AgS_9]$ is also

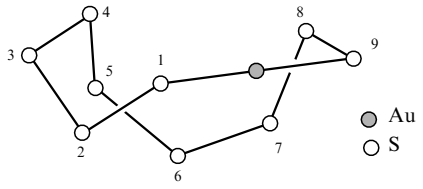


Figure 8. Structure of the $[AuS_9]^-$ anion.[48]

known.[29] However, the anions in the crystal of this salt are substantially disordered.

Finally, let us consider a few examples of molecular polytellurides, which are presently known only for gold. In 1985, the first gold polytelluride $(Ph_4P)_4[KAu_9Te_7]$ containing isolated cluster ions was described.[49] The reaction of a methanolic solution of K_2AuTe_2 with a solution of Ph_4PBr afforded an orange precipitate. Additional treatment of the latter with DMF and a solution of Ph_4PBr in MeOH gave two products. One of them, which was isolated as triangular red platelet-like crystals, has the composition $(Ph_4P)_4[KAu_9Te_7]$. The structure of the $[KAu_9Te_7]^{4-}$ anion (Fig. 9) can be considered as that derived from the cubic structure of the above-described $[M_{12}S_8]^{4-}$ ions (M = Cu or Au) in which one vertex and three edges are removed. The ideal cubic structure is distorted due to the contraction along the threefold axis passing through the absent vertex and the centre of the ion. This contraction is responsible for the pronounced Au—Au interaction. The Au—Au distances in the triangles (see Fig. 9) vary from 0.3039 to 0.3221 nm. The average distance (0.313 nm) is close to the Au—Au distance in metallic gold (0.288 nm) and is substantially shorter than that in the hypothetical $[Au_{12}Te_8]^{4-}$ ion (0.363 nm). Like $[NaAu_{12}Se_8]^{3-}$, the $[Au_9Te_7]$ framework incorporates the encapsulated potassium ion, the Au—K distances being shorter than the Au—Te distances, which reflects the higher electronegativity of gold compared to that of tellurium (2.4 and 2.1, respectively). It is believed that the above-described encapsulation is responsible for the formation of a cryptand with this composition because the K^+ ion is too large to be encapsulated into the hypothetical $[Au_{12}Te_8]^{4-}$ ion.

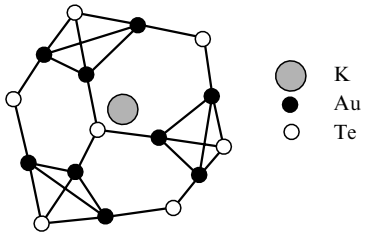


Figure 9. Structure of the $[KAu_9Te_7]^{4-}$ anion.[49]

The electrochemical preparation of the $(Ph_4P)_2[Au_2Te_4]$ and $(Bu^n_4N)_3[Au_3Te_4]$ salts with the use of $AuTe_2$ as the electrode was reported in a study.[50] The $[Au_3Te_4]^{3-}$ anion is gold(I) telluroditelluride (Fig. 10 *a*) and the $[Au_2Te_4]^{2-}$ anion is gold(I) bistelluride (Fig. 10 *b*). In both cases, the gold atoms have a linear coordination typical of Au^+ ions. However, the tendency for the trigonal coordination through the Au—Au bonds is also pronounced. The lengths of these bonds (see Fig. 10 *a*, *b*) are only slightly larger than the Au—Au distances in metallic gold.

Treatment of gold tellurides KAuTe and K_3AuTe_2 with ethylenediamine or DMF afforded salts containing the $[Au_2(Te_2)_2]^{2-}$ and $[KAu_9Te_7]^{4-}$ anions and the $[K_2Au_4Te_4]^{2-}$ anion in which the $[Au_4Te_4]^{4-}$ rhombi are linked in infinite stacks through the K^+ ions.[49,51]

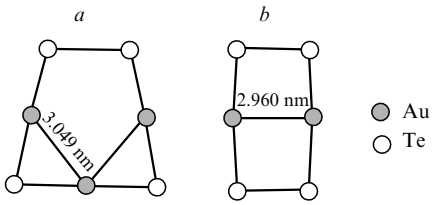


Figure 10. Structures of the $[Au_3Te_4]^{3-}$ (*a*) and $[Au_2Te_4]^{2-}$ (*b*) anions.[50]

The reaction of AuCN with polytellurides Te_n^{2-} in DMF in the presence of PEt_3 and NEt_4Cl yielded the $(NEt_4)_3[AuTe_7]$ salt.[52] The $[AuTe_7]^{3-}$ anion is planar, which is typical of Au(III) complexes (Fig. 11 *a*). The fact that the degree of oxidation of gold is equal to +3 is indirectly supported by the Au–Te bond lengths (0.2638–0.2664 nm), which are comparable with those in the known Au(III) compounds, for example, in AuTeI (0.2642–0.2684 nm), and is also confirmed by the data of Mössbauer spectroscopy on ^{197}Au nuclei. Hence, the anion under consideration is bisditelluridotritelluridoaurate(III).

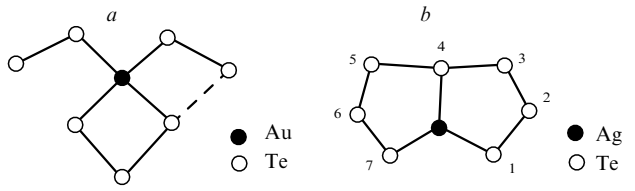


Figure 11. Structures of the $[AuTe_7]^{3-}$ (see Ref. 52) (*a*) and $[AgTe_7]^{3-}$ (*b*) anions.[54]

The structure of the analogous silver complex $[AgTe_7]^{3-}$ isolated as the $(Ph_4P)_2(Et_4N)[AgTe_7]$ salt (Fig. 11 *b*)[53,54] differs from that of the $[AuTe_7]^{3-}$ anion. In this silver complex, the Ag^+ ion adopts a trigonal coordination. Based on the charge of the $[AgTe_7]^{3-}$ anion, the charge of −4 should be assigned to the ligand and the ligand can be considered as η^3-Te_7^{4-}. The Te(4)–Te(5) and Te(4)–Te(3) bond lengths (0.2866 and 0.3230 nm, respectively) are substantially different, whereas this difference in the corresponding bonds in the analogous $[HgTe_7]^{2-}$ complex is insignificant (0.3050 and 0.2997 nm, respectively[53]). Therefore, the nature of the bonds in the new polytelluride η^3-Te_7^{4-} ligand is still unknown. Polyhalide ions, in particular, such as I_8^{2-}, are the closest analogues of this ligand. The concept of hypervalence is used for describing the nature of bonds in these compounds, in particular, in S_2N_2, S_4N_4, polyhalides, xenon halides, *etc*.[55] In accordance with this concept, the Te(3)–Te(4)–Te(5) bond can be considered as a three-centre four-electron bond, whereas the Te(2)–Te(3) and Te(5)–Te(6) bonds are usual two-centre two-electron bonds.

Copper and silver tetratellurides containing the $[Te_4M(\mu\text{-}Te_4)MTe_4]^{4-}$ ions (M = Cu or Ag) were also prepared.[56] The structures of these ions are similar to that of the $[S_6Cu(\mu\text{-}S_8)CuS_6]^{4-}$ ion. In these tellurides, the copper(I) and silver(I) atoms are trigonally coordinated through the chelating and bridging Te_4^{2-} ions.

III. Coordination polymers based on polychalcogenides of Group IB elements

Coordination polymeric polychalcogenides are intermediate between low-molecular-weight polychalcogenides and chalcogenides containing only X^{2-} and/or X_2^{2-} ions. These ions are bound to metal ions through substantially covalent bonds due to which these compounds are virtually insoluble in the usual organic solvents.

Polymeric polychalcogenides containing the $[CuS_4]^-$ anion have been known since the early 20th century.[57] However, their structures were established only late in the 1980s. Generally, polymeric polychalcogenides were prepared from solutions. However, the procedure for the synthesis of these compounds from melts of alkali metal polychalcogenides, which act simultaneously as the solvent and the reagent, was proposed in 1989.[58] This method appears to be more promising and allows one to prepare more perfect single crystals suitable for X-ray diffraction study. Coordination polymeric polychalcogenides can be synthesised in the temperature range of 150–350 °C. At lower temperatures, molecular polychalcogenides are obtained. At higher temperatures, mono- and dichalcogenides of Group IB metals are formed.

Oxidation of copper in a melt of K_2S_4 at 215 and 250 °C affords two modifications (α and β, respectively) of the $K[CuS_4]$ salt. These modifications are insoluble in usual organic solvents and stable to hydrolysis and oxidation with atmospheric oxygen. Both phases have quasi-one-dimensional structures (Fig. 12).

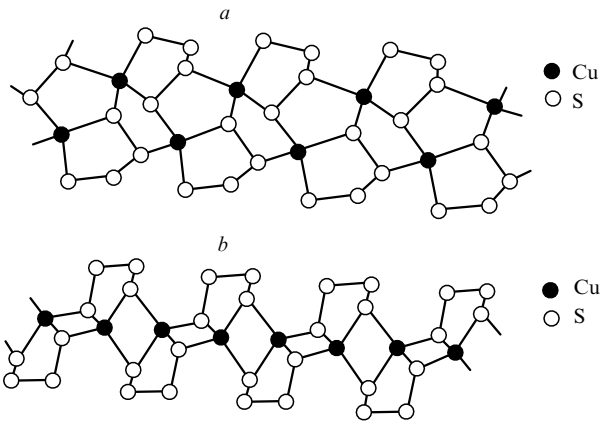


Figure 12. Infinite α-$[Cu(S_4)]_n^{n-}$ (*a*) and β-$[Cu(S_4)]_n^{n-}$ (*b*) chains.[58]

The α-$K[CuS_4]$ salt is isostructural to the $(NH_4)[CuS_4]$ salt described previously[59] and contains the tetrasulfide ligands chelating the copper(I) ions (Fig. 12 *a*). The $[CuS_4]^-$ ions form infinite noncentrosymmetrical chains extended along the *a* axis. These chains can be considered as a sequence of fused five-membered CuS_4 and Cu_2S_3 rings. Therefore, the S_4^{2-} ion in this structure plays the unprecedented role of a bridge that links three Cu^+ ions.

The structure of β-$K[CuS_4]$ contains centrosymmetrical one-dimensional β-$[CuS_4]_n^{n-}$ chains with a nearly linear (the CuCuCu angle is 173.5 °) arrangement of the copper atoms linked through the bridging S_4^{2-} ligands (Fig. 12 *b*). Unlike the α-phase, the β-$[CuS_4]_n^{n-}$ chains consist of the five-membered (CuS_4) and four-membered (Cu_2S_2) rings. Since the β-modification is formed at higher temperature, it can be suggested that this phase is thermodynamically more stable. Heating of crystals of α-$K[CuS_4]$ above 250 °C results in transition to the β-phase. However, cooling of crystals of the β-phase do not lead to the reverse transition. The K_2S_4 solvent is of considerable importance in the α → β-transition. Heating of crystals of α-$K[CuS_4]$ in the absence of the solvent *in vacuo* resulted in their decomposition to CuS and K_2S_x.[58]

Treatment of an alkaline solution of the $(NH_4)[CuS_4]$ salt with solutions of salts containing bulky cations afforded low-molecular-weight polysulfides, for example, $(NMe_4)_2[Cu_4(S_6)_3]\cdot 4H_2O$, $(Et_3NBn)_2[Cu_4(S_4)(S_5)_2]\cdot 4H_2O$ and $(Ph_3PBn)_2[Cu_6(S_6)_4]\cdot \cdot 12H_2O$.[60] The authors failed to prepare single crystals suitable for X-ray diffraction study and hence, the formulas were proposed by analogy with the known $[Cu_4(S_4)_x(S_5)_{3-x}]^{2-}$ and $[Cu_6(S_4)_3(S_5)]^{2-}$ salts.[31,35,36] Metal cations bulkier than alkali

metal cations were used, apparently, with the aim of achieving more complete isolation of depolymerisation products from solutions.

The $[(NH_3)_2C_2H_4][CuS_5]_2 \cdot 4H_2O$ salt was synthesised as orange-red single crystals.[61] In the $[CuS_5]_n^{n-}$ anion formed as an infinite sequence of the $-Cu-S-Cu-S-$ bonds, each S_5^{2-} ion links three Cu^+ ions (Fig. 13). Therefore, the $[CuS_5]_n^{n-}$ chains consist of the five-membered CuS_4 and Cu_2S_3 rings. Analogous anionic chains were also observed in the crystals of the $(NMe_4)[AgS_5]$ [62] and $(NMe_4)[AgSe_5]$ salts.[63]

These examples demonstrate that the properties of the above-described polysulfides are relatively independent of the nature of the outer-sphere cations.

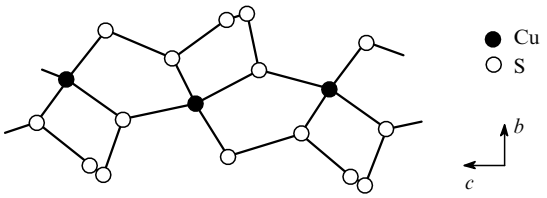


Figure 13. Infinite $[CuS_5]_n^{n-}$ chains.[61]

Treatment of copper with a melt of cesium polysulfide with composition Cs_2S_{11} at 270 °C afforded the $Cs[CuS_6]$ salt.[64] In the crystal, the $[CuS_6]^-$ anions form one-dimensional centrosymmetrical $[CuS_6]_n^{n-}$ chains (Fig. 14) separated by Cs^+ ions. The Cu^+ ions are chelated by the terminal sulfur atoms of the S_6^{2-} ions to form the seven-membered CuS_6 rings. In this case, the terminal sulfur atoms of the S_6^{2-} ion each act also as a bridge between the adjacent copper atoms resulting in the formation of the four-membered Cu_2S_2 rings. The $Cs[CuS_6]$ salt is one of a few examples of coordination polymers containing such long polychalcogenide ions.

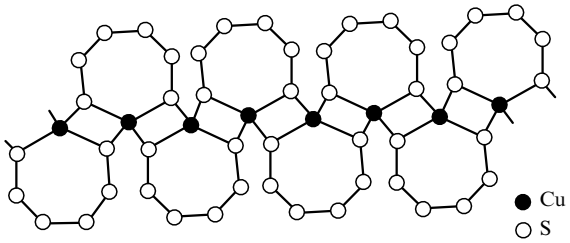


Figure 14. Infinite $[CuS_6]_n^{n-}$ chains.[64]

In the crystals of the $\{(Ph_4P)[AgSe_4]\}_n$ salt, the trigonal coordination about the silver(I) atom is formed by the Se_4^{2-} ions. However, only five-membered rings occur in this case (Fig. 15). Only one of the terminal selenium atoms of the Se_4^{2-} ion acts as a bridge.[65]

Polymeric silver selenides with stack structures were prepared with the use of ethylenediamine in the supercritical state as the solvent:[66, 67]

$$K_2Se_4 + 3Se + 12Ag \xrightarrow{350\ ^\circ C} K_2Ag_{12}Se_7.$$

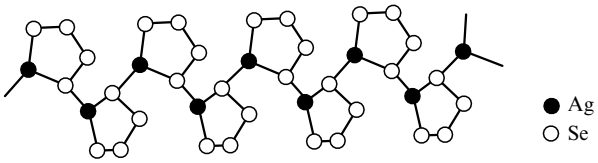


Figure 15. Infinite $[Ag(Se_4)]_n^{n-}$ chains.[65]

The crystals of $K_2Ag_{12}Se_7$ contain the 18-membered $Ag_{12}Se_6$ rings. The seventh Se^{2-} ion occupies the centre of this ring. In the crystal structure, the rings are packed in stacks resulting in the formation of channels. These channels are occupied by K^+ ions. The sulfide with the same composition, which was prepared under analogous conditions, has quite a different structure.[68]

Oxidation of gold with a melt of potassium polyselenides at 250 °C afforded polymeric gold polyselenides $KAuSe_5$ and K_3AuSe_{13} containing the $[AuSe_5]_n^{n-}$ and $[AuSe_{13}]_n^{3n-}$ ions, respectively.[69]

Unlike the analogous copper and silver pentachalcogenides, the Au^+ ions in the $[AuSe_5]_n^{n-}$ anions are linearly coordinated (the SeAuSe angle is 179 °) by the bridging Se_5^{2-} ions (Fig. 16 *a*), the latter being coordinated only through the terminal selenium atoms. The structure of the $[AuSe_5]_n^{n-}$ ions is analogous to that of the $[AuSe]_n^{n-}$ ions with the formal replacement of the Se^{2-} ions by the Se_5^{2-} ions. The $[AuSe_5]_n^{n-}$ chains are linked through Au – Au interactions. The Au – Au distance (0.295 nm) is close to that in metallic gold (0.288 nm) and is substantially shorter than the corresponding distances in KAuSe [70] and in α- and β-AuSe.[69] Therefore, the presence of Au – Au contacts leads to dimerisation of polymeric $[AuSe_5]_n^{n-}$ ions. In this case, the gold atom has the d^{10} configuration and this dimerisation is one of a few examples of $d^{10}-d^{10}$ interactions. Formally, a combination of two filled *d*-orbitals of the gold atom gives bonding and antibonding orbitals resulting in the absence of a bond. However, it is known that the relativistic effects are essential in the case of heavy elements, such as gold,[71] and the reasoning regarding the electronic structures of silver complexes, which is based on the nonrelativistic approach, is incorrect. Pekka [71] examined the role of relativistic effects in studies of the structural molecular characteristics. If these effects are taken into account, the bond lengths are decreased, the value of this decrease being proportional to the square of the charge on the atomic nucleus and varying from 0.250 – 0.300 nm for AuH to 0.450 – 0.500 nm for Au_2. Correspondingly, the force constant and the dissociation energy of the Au_2 molecule increase by factors of more than four and two, respectively. The role of the relativistic effects decreases as the bond ionicity increases. Therefore, this role should be noticeable in gold chalcogenides in which the degree of covalence of the Au – X bonds is large. Dimerisation of the $[AuSe_5]_n^{n-}$ ions is a prominent example of this phenomenon.

The presence of these bonds between ions with closed shells was also described for other gold compounds, in particular, for the complex $[Au_2Se_5]^{2-}$ and $[Au_2Se_6]^{2-}$ anions,[72] and for the sulfide $Tl_2Au_4S_3$.[73] Since this phenomenon is unknown in the chemistry of other elements, it was suggested [72] that the term 'aurophilic attraction' to be used for the $Au^+ - Au^+$ interaction. The authors believed [72] that the aurophilic attraction is a result of correlation effects, which are ignored in the Hartree – Fock approximation.

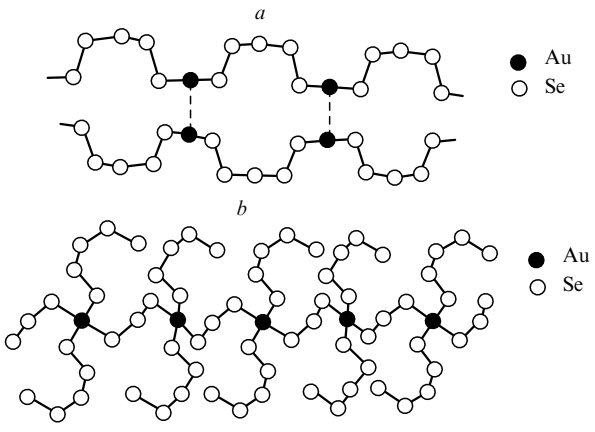
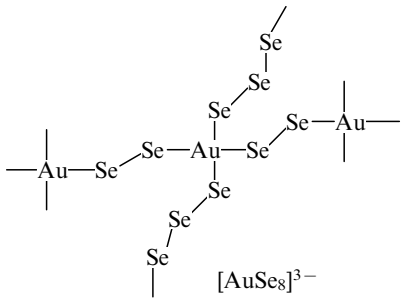


Figure 16. Structure of the $[AuSe_5]_n^{n-}$ (*a*) and $[AuSe_{13}]_n^{3n-}$ chains (*b*).[69]

However, the authors restricted themselves only to nonrelativistic calculations. Hence, the above-considered interpretation, in which the importance of the relativistic effects in chemistry was emphasised, is, admittedly, more reliable (see also the study [74]).

The $[AuSe_{13}]_n^{3n-}$ ion also has an unusual structure. This ion can be described as the catenabis(pentaselenido-μ-triselenido-aurate)(III) ion $[Se_5Au(\mu\text{-}Se_3)AuSe_5]_n^{3n-}$. This is the only known complex containing simultaneously the monodentate Se_5^{2-} ions and the bridging Se_3^{2-} ions coordinated to the Au^{3+} ions (Fig. 16 *b*).

The reaction performed under the same conditions (ethylenediamine in the supercritical state) with the use of sodium polyselenides instead of potassium polyselenides afforded Na_3AuSe_8.[75] The crystals of this complex contain polymeric chains formed by the planar-square Au^{3+} complexes. Two Se_3^{2-} ions are coordinated in a monodentate fashion.



The polymeric complexes $(Me_4N)[MTe_4]$ (M = Cu or Ag) containing tetratelluride ions were prepared for the first time in 1993.[43] These complexes, unlike the analogous tetrasulfides and tetraselenides, have layered structures (see Fig. 17). The layers consist of the five-membered MTe_4 rings. Each Te_4^{2-} ligand links three copper atoms. An interesting feature of this structure is the presence of cavities formed by 14-membered rings (see Fig. 17). The size of the cavity is determined by the shortest distances between the opposite tellurium atoms (0.6034 and 0.6195 nm). The $(Me_4N)[MTe_4]$ salts are diamagnetic semiconductors with the width of the forbidden band of 0.80 and 0.90 eV for M = Cu and Ag, respectively.

In attempting to prepare mixed copper sulfidotelluride complexes from melts of $Cs_2S_xTe_y$, the authors [64] isolated the $Cs_6Cu_2(S_6)_2(TeS_3)_2$ complex containing the dimeric $[Cu_2(S_6)_2(TeS_3)_2]^{6-}$ anion (Fig. 18). In this anion, two Cu^+ ions are chelated by two Se_6^{2-} ions (the seven-membered CuS_6 rings) and are linked to each other through two bridging TeS_3^{2-} ions. Only one sulfur atom of each TeS_3^{2-} ion is involved in coordination, *i.e.*, the four-membered Cu_2S_2 rings are formed. The trithiotellurite ion differs sharply in this property from the isoelectronic SO_3^{2-} ion.

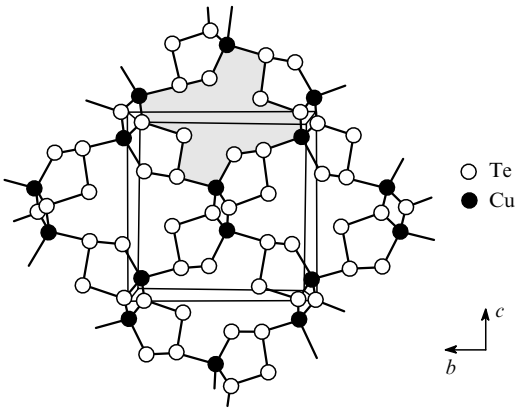


Figure 17. Structure of the $[CuTe_4]^-$ layers.[43] One of the 14-membered rings is hatched.

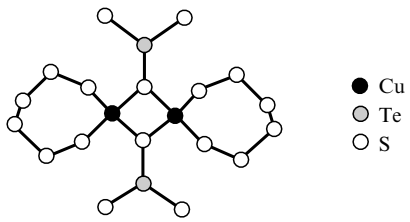


Figure 18. Structure of the $[Cu_2(S_6)_2(TeS_3)_2]^{6-}$ ion.[64]

Unfortunately, successful attempts to prepare mixed selenidotelluride complexes are as yet unknown although their syntheses are quite possible because selenium and tellurium differ in properties to a lesser degree than sulfur and tellurium. For example, mixed sulfidoselenide complexes were formed in the α-$CsCu(S_xSe_{4-x})$ and $CsCu(S_xSe_{6-x})$ systems.[76]

IV. Chalcogenides containing only X^{2-} and/or X_2^{2-} ions

The majority of compounds of this type give crystals with essentially covalent M—X bonds. Many of these compounds possess metallic properties and exhibit superconducting properties at low temperatures (Table 1). According to the RVB theory,[5–9] the metallic state in these crystals can occur on condition that the metal atoms exhibit a mixed valence.

It is well known that the simplicity of the electronic structures of chalcogenides, such, for example, as CuS or CuS_2, is more apparent than real. Thus, according to the X-ray diffraction data, the formula $Cu_4^+Cu_2^{2+}(S_2^{2-})_2(S^{2-})_2$ should be assigned to covelline CuS, *i.e.*, both the metal and chalcogen atoms in this compound exhibit mixed valences.[17] However, after the results of the study performed by Jellinek were reported,[77] the question about the electronic structures of copper chalcogenides became a matter of discussion. Based on the results of X-ray photoelectron spectroscopy, Jellinek assigned the degree of oxidation of +1 to the copper atoms in all chalcogenides (for example, in CuS, CuSe, CuTe, CuS_2, KCu_4S_3, *etc.*). To satisfy the principle of electronegativity of the salts, Jellinek had to represent the structures of the copper chalcogenides by formulas, which are absurd from the chemical standpoint, such as, for example, Cu^+Te^- for CuTe, $Cu_3^+(S_2^{2-})S^-$ for CuS or $K^+Cu_4^+S_2^{2-}S^-$, where S^- and Te^- are nothing but radical ions, which should be dimerised to the S_2^{2-} and Te_2^{2-} ions, respectively. I do not share the opinion of Jellinek and believe that one of the reasons for the absence of lines from the Cu^{2+} ions in the X-ray photoelectron spectra [77] is a mistake in the procedure for the preparation of samples. Thus, ground samples of the dichalcogenides were applied to the freshly purified surface of indium. In this case, it is quite possible that the chalcogenide reacted with indium as a result of which Cu^{2+} was reduced to Cu^+ on the surface:

$$Cu^{2+} + In \longrightarrow Cu^+ + In^+.$$

The authors [77] did not perform subsequent treatment of the surface of the samples under study with Ar^+ ions (to remove the surface layer containing the adsorbed molecules) until this treatment ceased to affect the spectral patterns. Note also that the formulas proposed by Jellinek do not allow one to explain the fact that the above-mentioned chalcogenides possess the metallic conductivity. Since both the Cu^+ and S_2^{2-} ions have filled electron shells, only the S^- ions (actually, these ions are the $S^{-\cdot}$ radical anions) can be responsible for the charge transfer. Interactions between the orbitals of the adjacent $S^{-\cdot}$ species would necessarily lead to the formation of the covalent bond

$$2S^{-\cdot} \longrightarrow S_2^{2-},$$

and hence, the formulas proposed by Jellinek would be more properly written as $Cu_2^+(Te_2^{2-})$ or $Cu_6^+(S_2^{2-})_3$. However, in this

case, the copper chalcogenides would exhibit dielectric properties and, moreover, the above-considered formulas are contradictory to the structural data.[17]

The fact that the approach proposed by Jellinek is inadequate gave impetus to the more accurate determination of the structure of CuS. Thus, Gotsis *et al.*[78] attempted to redetermine the structure of CuS by the high-resolution X-ray powder diffraction method and calculated the electronic structure using density functional theory. Based on the results obtained, the authors reasoned that the $Cu^+ - S_2^{2-} - Cu^+$ formula is more realistic for CuS (the authors believed that this formula is also appropriate for CuSe). However, this interpretation of the charge state of CuS suffers from drawbacks analogous to those of Jellinek's interpretation. Liang and Whangbo[79] believed that the $Cu_3^+(S_2^-)S^{2-}$ formula is more adequate than the formula suggested by Jellinek $[Cu_3^+(S_2^{2-})S^-]$. Although the authors noted the substantially covalent character of the Cu–S bond, they concluded that holes in the valence band are associated with oxidation of only sulfur, *i.e.*, the authors did not assume the mixed-valence state for copper.

A study[80] was devoted to the electronic structures of copper chalcogenides and their relationship with the conductivity. The authors calculated the electronic structures of copper sulfides with the use of the extended Hückel method and demonstrated that holes are approximately equally distributed over copper and sulfur atoms due to substantial overlap between the 3*p* orbitals of the sulfur atoms and the 3*d* orbitals of the copper atoms. This indicates that the classical formula for CuS is more realistic and, as will be seen from the data given below, agrees with the existence of charge density waves (CDWs) in conducting chalcogenides based on copper.

The X-ray photoelectron spectra of samples of highly pure CuS, which was synthesised according to a procedure reported in the handbook,[81] have lines at 932.2 and 933.7 eV with the intensity ratio of 1.3 : 1.[10] These lines correspond to the energies of the $2p_{3/2}$ levels of copper [ECu($2p_{3/2}$)]. The first and second lines can be assigned to the Cu^+ and Cu^{2+} ions, respectively. Note that the ECu($2p_{3/2}$) value given for CuS (932.8 eV) in the handbook[82] is the average of the values determined in the study.[10] Jellinek[77] reported an obviously unrealistic value of 931.4 eV, which is even smaller than that for Cu_2S (*cf.* 932.0 eV[77] and 932.9 eV[82]).

To summarise, it can be noted that the problem of the determination of the charge state of copper in chalcogenides is in essence identical to that for oxide HTSCs based on copper. However, in the case of chalcogenides the situation is more complex because the Cu–X bonds in these compounds are more covalent that those in the corresponding oxides.

Taking into account the complexity and ambiguity of the determination of charge states of the copper and chalcogen atoms in chalcogenides, hereinafter the following approach will be used.

Chalcogenides are considered to be compounds of monovalent copper if the sum of the degrees of oxidation of the cations is equal to twice the number of the chalcogen atoms (*i.e.*, on the assumption that the degrees of oxidation of the chalcogen and copper atoms are -2 and $+1$, respectively). If this sum is smaller than twice the number of the chalcogen atoms, chalcogenides are considered as mixed-valence compounds in which the degree of oxidation of copper is larger than $+1$ and the degree of oxidation of chalcogen is larger than -2. Thus, according to this approach, sulfide $NaCu_5S_3$ contains the Cu^+ and S^{2-} ions, whereas sulfide $NaCu_4S_3$ is a mixed-valence compound. This approach is known in the literature as Zintl's concept (according to Ref. 83).

Ternary copper chalcogenides can be divided into two groups: compounds with chain structures and compounds with layered structures. At the same time, according to the above-proposed approach, these compounds can be separated into copper(I) chalcogenides and mixed-valence copper chalcogenides (the degree of oxidation of copper is larger than unity). The fruitfulness of this approach is apparent. Thus, virtually all copper(I) chalcogenides are semiconductors, whereas mixed-valence copper chalcogenides possess the metallic conductivity.

All chalcogenides of the general formula $MCu_{2n}X_{n+1}$ (where M is alkali metal, X is chalcogen, $n = 1-3$) have layered structures. The following layered ternary copper chalcogenides are known: $TlCu_2Te_2$,[80] $TlCu_2Se_2$,[84] $TlCu_2S_2$, $TlCu_2SeS$,[85] $TlCu_4S_3$, $TlCu_4Se_3$,[80,86] KCu_4S_3,[87] KCu_4Se_3,[86] $RbCu_4S_3$,[88] $RbCu_4Se_3$, $CsCu_4S_3$, $CsCu_4Se_3$[86] and $TlCu_6S_4$.[89] Since the total charge of the cations in the compounds of this series is one less than twice the number of the chalcogen atoms, these chalcogenides should be considered as mixed-valence compounds. It is therefore concluded that the valence band contains holes. Hence, these chalcogenides should exhibit metallic properties.

Selenide $TlCu_2Se_2$ was prepared[84] by heating (< 1050 °C) stoichiometric amounts of TlSe, copper and selenium *in vacuo* followed by slow cooling. The crystals of $TlCu_2Se_2$ consist of the Cu–Se layers. The Tl^+ ions are located above and below the layers. The Cu–Se bonds within the layers are substantially covalent. The copper atoms are located inside the tetrahedra formed by the selenium atoms, only three-fourths of positions being occupied (the $ThCr_2Si_2$ structural type) (Fig. 19).

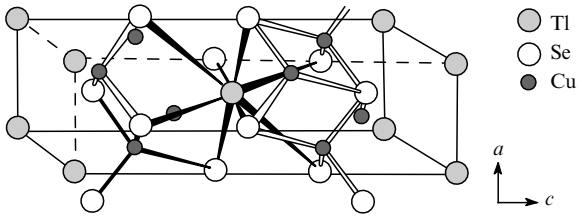


Figure 19. Crystal structure of $TlCu_2Se_2$.[90]

It was found[90] that the $TlCu_2Se_2$ salt exhibits metallic properties. To account for this fact, Brun *et al.*[90] assumed the coexistence of Tl(I) and Tl(III) selenides in the lattice. However, this assumption is contrary to the structural data and the results of electrophysical measurements.[91] Selenide $TlCu_2Se_2$ possesses the rather high conductivity ($\rho_{RT} = 5 \times 10^{-5}$ Ω cm). The temperature dependence of the conductivity, which was measured down to liquid helium temperature, is typical of metals. No substantial difference between the conductivities measured for single crystals and for pressed powders of $TlCu_2Se_2$ was observed, which is indicative of the weak anisotropy of the resistance of crystals. For $TlCu_2Se_2$, the Hall effect was measured and it was demonstrated that this selenide is a metal with hole conductivity (one hole per formula unit, like in the isostructural $TlCu_2Te_2$ compound[91]). This fact rules out the existence of two forms of thallium suggested in the study[90] because if this were the case, electrons, which fill the conduction band, would act as carriers.

Isostructural sulfide $TlCu_2S_2$ was prepared by Berger.[85] Thus, heating a one-phase sample of Tl_4S_3, which has been synthesised beforehand, with powdered copper and sulfur afforded $TlCu_3S_2$ the subsequent treatment of which with a concentrated ammonia solution and a 30% H_2O_2 solution yielded $TlCu_2S_2$. This compound is unstable[85] and reversibly decomposes to three phases, *viz.*, to TlCuS, $TlCuS_2$ and $TlCu_4S_3$, on heating to 330 K.

Sulfide $TlCu_2S_2$, like the selenide and telluride, exhibits metallic properties.

Later on, chalcogenides $TlCu_2X_2$ (X = S or Se) and mixed chalcogenide $TlCu_2SSe$ were prepared[92] and studied by X-ray photoelectron spectroscopy. According to Jellinek's concept, the authors[92] assigned the degree of oxidation of $+1$ to the thallium and copper atoms in $TlCu_2SSe$. The X-ray photoelectron spectrum of this compound has two lines in the ECu($2p_{3/2}$) region. The authors attributed these lines to the difference in the environment about the copper atoms and suggested that one line belongs to the copper atom bound to the selenium atom and the second line belongs to the copper atom bound to the sulfur atom. However, this assignment of the lines implies the structural ordering in the

crystals of the mixed chalcogenide and the equality of the two lines, which was not observed experimentally.

The metal–nonmetal transition should occur on addition of one electron to the valence band of chalcogenide MCu_2X_2 (M is alkali metal) because the valence band becomes completely filled. Actually, the replacement of alkali metal by alkaline-earth metal causes this transition and chalcogenides $BaCu_2S_2$ and $BaCu_2Se_2$ exhibit dielectric properties.[83, 93–95]

Single crystals of $BaCu_2X_2$ develop an orange colour in transmitted light and a metallic-black colour in reflected light, which is characteristic of semiconductors. In the study,[93] chalcogenides $BaCu_2X_2$ were prepared by heating stoichiometric amounts of barium and copper chalcogenides with metallic copper. In this case, orthorhombic crystals with a chain structure were formed.

Sulfide $BaCu_2S_2$ was prepared by the reaction of $BaCO_3$ and CuO with sulfur at 700 °C under a stream of CS_2.[94] However, this procedure afforded the tetragonal phase of $BaCu_2S_2$,[95] which has the layered structure[83, 95] analogous to the structure of $TlCu_2X_2$ (the $ThCr_2Si_2$ structural type).

The conductivity of sulfide $BaCu_2S_2$ was measured[96] and this compound was found to exhibit metallic properties in the range of 40–293 K. This result is difficult to explain on the basis of the accepted notion of the electronic structure of chalcogenides because sulfide $BaCu_2S_2$ does not contain holes in the valence band and can be represented by the formula $Ba^{2+}Cu_2^{+}S_2^{2-}$. At the same time, it was demonstrated[83] that this compound exhibits semiconducting properties at 77–293 K. This discrepancy in the results was accounted[83] for by the procedure for the synthesis used in the study,[96] which afforded a mixture of $Ba_{0.96}Cu_{2.01}S_{1.94}$ and $Ba_{0.95}Cu_{3.91}S_{2.97}$ in a ratio of 17 : 3. The resistance of the sulfide increases insignificantly (by a factor of ~ 2.7) as the temperature decreases from 300 to 77 K, from which an approximate estimate of the activation energy can be obtained ($E_a \sim 0.01$ eV). This estimate was not made in the study.[83] For $BaCu_2S_2$, the magnetic susceptibility was measured and the superconductivity was found to be absent to 2 K. The temperature dependence of the magnetic susceptibility is described by the following equation

$$\chi_{exp} = \frac{C}{T} + \chi_{dia} + \chi_0 ,$$

where C is the Curie constant, χ_{dia} is the diamagnetism of the core and χ_0 is the temperature-independent paramagnetism. Judging from the value of the Curie constant ($C = 5.83 \times 10^{-3}$ emu K mol^{-1}), the paramagnetic contribution results from admixtures whose concentration was $\sim 1.5\%$ and $BaCu_2S_2$ possesses diamagnetic properties. Hence, Zintl's concept appears to be true for both polymorphous modifications of $BaCu_2S_2$, which justifies its use in the present review.

Chalcogenides NaCuSe, NaCuTe, KCuSe, KCuTe[97] and KCuS[98] in which the degrees of oxidation of the copper and chalcogen atoms are +1 and −2, respectively, are similar in electronic properties to $BaCu_2X_2$. In spite of the formal similarity, these compounds have different structures. Thus, chalcogenides NaCuSe and NaCuTe belong to the PbFCl structural type, whereas KCuS, KCuSe and KCuTe belong to the Ni_2In structural type (contain zigzag Cu−S chains). The authors related this change in the structural type caused by the replacement of sodium by potassium to the difference in the ionic radii and noted that this change is unusual because only intermetallic compounds rather than salts belong to the Ni_2In structural type. These chalcogenides, judging from their colour, are narrow-band semiconductors. All these compounds were isolated as bright black crystals.

Chalcogenides of the general formula MCu_4X_3 (M is alkali metal and X = S or Se) were described for the first time by Rüdorff.[99] He isolated the KCu_4S_3 and $RbCu_4S_3$ salts. The $CsCu_4S_3$[88] and $TlCu_4S_3$[86] salts and the selenium analogues MCu_4Se_3 (M = Tl, K, Rb or Cs)[86] were described. The majority of these compounds were synthesised according to Rüdorff's carbonate method. Copper and chalcogen were mixed with carbonate of the corresponding metal and the mixture was heated to 650–700 °C. The resulting product was isolated as platelet-like black crystals. The thallium salts were synthesised with the use of Tl_2S or TlSe. Unlike the sulfide, the selenide $CsCu_4Se_3$, which was prepared according to the carbonate method, was not a one-phase compound.[86] The KCu_4Se_3 salt was prepared[86] also by fusing stoichiometric amounts of K_2Se, Cu and Se in a sealed evacuated quartz tube at 800 °C.

All the above-mentioned chalcogenides have layered structures. The double layers consist of sulfur atoms, which form tetrahedra linked *via* shared edges. The copper atoms are located inside the tetrahedra and the alkali metal or thallium atoms are located between layers. Due to mutual repulsions between the like-charged $[Cu_4X_3]_n^{n-}$ layers, it is required by the sizes of the M^+ ions that the M−X distances will be larger than the sum of their ionic radii. Thus, the Na^+ ion is too small to screen mutual repulsions between the layers and hence, $NaCu_4X_3$ salts do not exist.

Goodenough (according to Ref. 86) suggested the $D_0(n, l)$ criterion, which depends on the electronic configuration of the metal atom and the nature of the bridging ligand. This criterion determines the possibility of the nonmetal–metal transition. According to this criterion, Cu^{2+} sulfide complexes with the d^9 configuration can exhibit metallic properties if the internuclear distances Cu−Cu < 0.31 nm. In sulfide KCu_4S_3, four Cu−Cu distances are 0.276 nm and one Cu−Cu distance is 0.297 nm. These data satisfy Goodenough's criterion well and, consequently, KCu_4S_3 can exist in the metallic state. Hence, taking into account also the mixed-valence state of the copper and chalcogen atoms (the formal degree of oxidation of copper is +1.25), it can be suggested that chalcogenides MCu_4X_3 are metals. Actually, as early as 1952 Rüdorff found[99] that KCu_4S_3 and $RbCu_4S_3$ exhibit metallic properties. According to Rüdorff, the specific resistance ρ_{RT} of KCu_4S_3 and $RbCu_4S_3$ at ~ 20 °C is 2.5×10^{-2} and 1.67×10^{-2} Ω cm, respectively.

Later on, the major metallic state of KCu_4S_3 was confirmed:[87] $\rho = 2.5 \times 10^{-4}$ and 1.67×10^{-5} Ω cm at 293 and 20 K, respectively. The specific resistance changes linearly with temperature throughout the temperature range. Sulfide KCu_4S_3 exhibits temperature-independent paramagnetism (Pauli paramagnetism) and shows metallic reflection in the visible and near UV regions. Rüdorff obtained higher values of the electrical resistance because he performed measurements with the use of the double-contact method, which ignored the thermoelectromotive force.

In 1983, it was established[100] that other alkali thiocuprates MCu_4S_3 also exhibit metallic properties. Their electrical resistance changes linearly with temperature in the range of 150–300 K. At ~ 293 K, the resistance is 6.25×10^{-4}, 7.14×10^{-4} and 8×10^{-4} Ω cm for KCu_4S_3, $RbCu_4S_3$ and $CsCu_4S_3$, respectively. All three salts show temperature-independent paramagnetism.

Selenide $CsCu_4Se_3$ was prepared[101] by the hydrothermal synthesis. Alkali metal polyselenide M_2Se_x (M = Na or K; x = 2, 4 or 5), CsCl and copper were placed in a tube with water. The tube was evacuated, sealed and heated at ~ 120 °C for five days. Needle-like crystals of α-$CsCuSe_4$ and platelet-like crystals of $CsCu_4Se_3$ were isolated from the reaction mixture. The increase in the temperature to 170 °C resulted in an increase in the yield of $CsCu_4Se_3$ to 80% but the compound was formed as polycrystals. The Cu−Cu distances in selenides MCu_4Se_3 (0.2895 and 0.3071 nm[101]) satisfy Goodenough's criterion. Hence, taking into account also the mixed-valence states of the copper and selenium atoms, these selenides can be considered as metals.

The crystal structures of the MCu_4X_3 salts[102] are characterised by the presence of octahedral cavities (one cavity per formula unit) between the $[Cu_4X_3]_n^{n-}$ layers. The size of the cavity is large enough for an additional copper atom to occupy this cavity. The insertion of copper atoms into the octahedral cavities should lead to annihilation of holes in the valence band and, consequently, should cause the metal–nonmetal transition. According to Zintl's

criterion, chalcogenide MCu_5X_3 contains the $M^+Cu_5^+X_3^{2-}$ ions with the closed shells. The electrochemical reaction

$$K^+[(Cu_t)_4S_3]^- + Cu^+ + e \underset{\text{generation of holes}}{\overset{\text{annihilation of holes}}{\rightleftharpoons}} K^+[(Cu_t^+)_4Cu_o^+S_3^{2-}] \quad (1)$$

metal (Pauli paramagnetism) — semiconductor (diamagnetic)

afforded [103] chalcogenide KCu_5S_3 (Cu_t and Cu_o are the copper atoms occupying the tetrahedral and octahedral positions, respectively); the back reaction, *viz*., anodic oxidation of KCu_5S_3, gave the initial sulfide KCu_4S_3. According to the X-ray diffraction data,[103] the tetragonal symmetry of the crystals is retained in the course of the reaction. The unit-cell volume decreases from 140.4×10^9 nm^3 for KCu_4S_3 to 129.6×10^9 nm^3 for KCu_5S_3 due to additional attractions between the charged layers caused by the copper ions occupying the octahedral cavities between the layers. The specific resistance increases from 7.34×10^{-4} Ω cm for KCu_4S_3 to 1.90×10^{-3} Ω cm for KCu_5S_3, the sign of the temperature resistance coefficient changing to minus, *i.e*., KCu_5S_3 is a semiconductor.

As mentioned above, the $NaCu_4S_3$ salt does not exist. However, the $Na_2Cu_4S_3$ and $NaCu_5S_3$ salts are known.[104, 105] Both these salts can be considered as analogues of the KCu_5S_3 salt, in which octahedral cavities are occupied either by Na^+ or by Cu^+ ions. The $NaCu_5S_3$ salt was prepared by the hydrothermal synthesis and the $Na_2Cu_4S_3$ salt was synthesised from a carbonate melt.

Crystals of $NaCu_5S_3$ belong to the hexagonal system (unlike tetragonal crystals of KCu_5S_3) (Fig. 20). There are two crystallographically nonequivalent copper atoms per asymmetric unit. The Cu(1) atoms are almost linearly coordinated by two sulfur atoms. The Cu(2) atoms are coordinated by three sulfur atoms (as in $Na_2Cu_4S_3$) to form a trigonal pyramid. The Cu(1) atoms each have four Cu(2) neighbouring atoms, whereas the Cu(2) atoms each are surrounded by six Cu(1) atoms. The Cu–Cu distances (0.27 nm) satisfy Goodenough's criterion. However, according to Zintl's criterion, both salts contain ions with closed shells and, consequently, the $NaCu_5S_3$ and $Na_2Cu_4S_3$ salts are, apparently, semiconductors. This is also true for selenide $TlCu_5Se_3$.[85]

Annihilation of holes in the valence band of MCu_4X_3 can be also induced by the replacement of alkali metal by alkaline-earth metal. Sulfide $BaCu_4S_3$ was prepared [106] by heating a mixture of BaS, copper and sulfur in a sealed evacuated tube at 800 °C as crystals, which develop a red colour in transmitted light and exhibit metallic lustre in reflected light. According to the X-ray diffraction data, these are two different phases, *viz*., the α and β phases. The α phase, which is stable at room temperature, is transformed into the β phase at 640 °C. Both phases belong to the orthorhombic system. Their structures are similar and consist of chains formed by the BaS_6 trigonal prisms linked to each other *via* shared triangular faces. The copper atoms form infinite zigzag chains in the α phase (Cu–Cu, 0.275 nm) and infinite linear chains in the β phase (Cu–Cu, 0.29 nm). In spite of the filled valence band (as follows from the formula $Ba^{2+}Cu_4^+S_3^{2-}$), the short Cu–Cu contacts are responsible for the noticeable conductivity ($\rho_{RT} = 0.2$ Ω cm) of the crystals of $BaCu_4S_3$, which is virtually independent of the temperature.

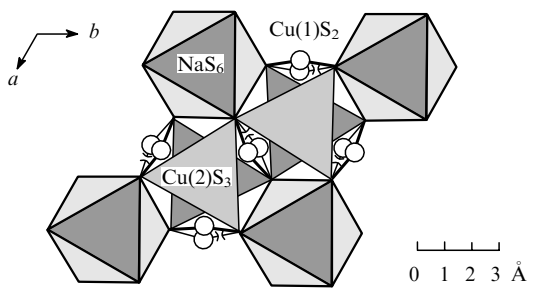


Figure 20. Crystal structure of $NaCu_5S_3$ projected onto (001). The NaS_6 octahedra (the Na atoms at $z/c = 1/4$ and 3/4), the linear coordination in $Cu(1)S_2$ (the Cu(1) atoms at $z/c = 1/4$ and 3/4) and the $Cu(2)S_3$ pyramids [the Cu(2) atoms at $z/c \sim 0$ and 1/2].

Only one salt belonging to the $MCu_{2n}X_{n+1}$ series with $n = 3$ is known, *viz*., $TlCu_6S_4$.[89] This salt was prepared by fusing a mixture of Tl_2S, copper and sulfur in a quartz tube. Its structure is similar to those of the preceding members of the series with $n = 1$ or 2. The crystal contains layers consisting of the CuS_4 tetrahedra alternating with layers of the thallium atoms. The $TlCu_6S_4$ salt should exhibit metallic properties because it is a mixed-valence compound with the Cu–Cu distances of 0.2783 and 0.2917 nm. Actually, the electrical resistance of single crystals of $TlCu_6S_4$ varies (although not quite linearly) proportional with temperature. The crystals are characterised by a plus sign of the Hall constant. The concentration of holes was determined from this constant (+1.29 per formula unit). Berger and Eriksson [89] noted that the effective radius of sulfur increases in the series $TlCu_{2n}S_{n+1}$ as n increases and related this effect to a change in the concentration of holes in the valence band per sulfur atom. A decrease in the ratio from +0.5 at $n = 1$ to +0.25 at $n = 3$ correlates with an increase in the radius (the closer the charge of sulfur to −2, the larger the radius). This interpretation is reasonable. However, from this interpretation it does not follow that holes are localised exclusively on the sulfur atoms.

In chalcogenides $TlCu_7X_4$ (X = S or Se), which are derivatives of the $TlCu_6S_4$ salts, additional copper atoms occupy cavities, which leads to filling of the valence band and causes the metal–nonmetal transition.[85] The mineral crookesite with composition $TlCu_{6.8}Se_4$, in which 80% of vacancies are occupied, possesses metallic properties [89] because the valence band is only partially filled (there are +0.2 holes per formula unit in the crystal).

The members of the MCu_6X_4 series are represented only by thallium salts. However, the ammonium analogue of $TlCu_7X_4$, *viz*., the $NH_4Cu_7S_4$ salt, is known. This salt satisfies Zintl's criterion and, consequently, has a filled valence band.[87] Judging from the Cu–Cu bond lengths (0.283 and 0.294 nm), this salt possesses semiconducting properties.

Since no salts of the $MCu_{2n}X_{n+1}$ series with $n > 3$ are available, the question of whether these salts can exist was considered theoretically.[80] The formal analogy of the reactions of the type

$$Cu_{2n}X_{n+1} + Cu_2X \longrightarrow Cu_{2(n+1)}X_{n+2}$$

was drawn to the so-called isodesmic reactions, which are well known in theoretical organic chemistry. In these reactions, the number of bonds of a particular type remains invariant, but their relative arrangement changes. For example,

$$CH_3CH_2CH_3 + CH_4 \longrightarrow 2CH_3CH_3.$$

It was demonstrated that this concept is applicable to two layers of the $Cu_{2n}X_{n+1}^{q-}$ anions ($q = 1$ or 2) and the energy effects of the isodesmic reactions with the participation of these anions were calculated (the extended Hückel method).[80]

$$Cu_2S_2^{q-} + Cu_2S \longrightarrow Cu_4S_3^{q-}, \quad (2)$$

$$Cu_4S_3^{q-} + Cu_2S \longrightarrow Cu_6S_4^{q-}, \quad (3)$$

$$Cu_6S_4^{q-} + Cu_2S \longrightarrow Cu_8S_5^{q-}. \quad (4)$$

Reaction	(2)	(3)	(4)
ΔE /eV ($q = 1$)	−0.320	−0.159	−0.061
ΔE /eV ($q = 2$)	−0.023	−0.002	0.000

The results of calculations are in complete agreement with the experimental data. Thus, these reactions are most favourable for compounds with $q = 1$, *viz.*,

$$MCu_{2n}X_{n+1} + Cu_2X \longrightarrow MCu_{2(n+1)}X_{n+2},$$

where M is a single-charged ion (alkali metal or thallium). These reactions are less favourable for analogous barium salts ($q = 2$). Thus, the absence of the $BaCu_6S_4$ salt is attributable to fact that the gain in energy is virtually absent for the reaction

$$BaCu_4S_3 + Cu_2S \longrightarrow BaCu_6S_4.$$

Judging from the very low energy of reaction (4), MCu_8S_5 salts, most probably, do not exist.

The absence of compounds of the $MAg_{2n}X_{n+1}$ series lends support to the validity of the approach, which we applied to the determination of the electronic structures of ternary copper chalcogenides. In these compounds, silver should possess mixed valence because the oxidation state of this element in chalcogenides is no greater than +1. However, when hydrogen sulfide was passed through a melt of $Ba[Ag(CN)_2]$ in a mixture with KNCS (500 °C, 30 min), the sulfide $BaAg_2S_2$ ($CaAl_2Si_2$ structural type), which meets Zintl's concept, was obtained.[107] The structure of $CaAl_2Si_2$ is characterised by the presence of the $[Al_2Si_2]^{2-}$ structural elements in which three crystallographically equivalent Si–Al bonds are shorter than the fourth bond directed along the *c* axis. An analogous situation was observed in the crystals of $BaAg_2S_2$, with the only difference that three equivalent S–Ag bonds (0.2686 nm) are longer than the fourth bond (0.2659 nm). The data on the conductivity were not reported in the study.[107] However, based on Zintl's concept and taking into account the dark-red colour of the crystals, it is believed that sulfide $BaAg_2S_2$ is a semiconductor.

Chalcogenides $K_2Ag_4S_3$[87, 110] (Fig. 21 *a*) and $K_2Ag_4Se_3$[109] (analogues of $Na_2Cu_4S_3$) as well as $RbAg_5S_3$[108] (an analogue of $NaCu_5S_3$) and $CsAg_7S_4$[108] (an analogue of $TlCu_7S_4$) satisfy Zintl's criterion. The $M_2Ag_6S_4$ salts (M = Na or K) containing an alkali metal atom instead of the seventh silver atom were reported.[66] These chalcogenides were prepared according to the carbonate procedure by heating a mixture of powdered silver, chalcogen and the corresponding alkali metal carbonate to 1000 °C for ~6 h. Since the resulting anthracite-like bright crystals are unstable in air, the authors[109] failed to isolate the $K_2Ag_4Se_3$ salt as single crystals suitable for X-ray diffraction analysis.

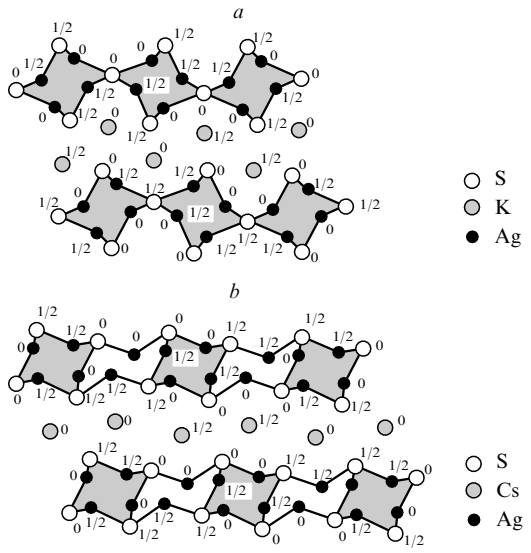


Figure 21. Projections of the structures $K_2Ag_4S_3$ (*a*) and $CsAg_3S_2$ (*b*) along the *b* axis.

The $RbAg_5S_3$ and $CsAg_7S_4$ salts were prepared as dark-red needle-like crystals according to the carbonate procedure by heating in an autoclave (~300 °C, 84 h) with the use of ethylenediamine in the supercritical state as the solvent.

The hexagonal crystals of $RbAg_5S_3$ contain the Ag_6S_6 twelve-membered rings in which the silver and sulfur atoms adopt the coordination number of 3. The rings are linked to each other through the silver atoms (the coordination number is 2) with the nearly linear coordination and are packed in stacks. The structure contains channels with a diameter of ~0.7 nm. These channels are occupied by the Rb^+ ions (Fig. 22). The Ag–Ag distances vary from 0.296 to 0.307 nm, which may indicate the presence of covalent interactions between the Ag^+ ions with the d^{10} configuration. It was noted[108] that the potassium analogue KAg_5S_3 has an analogous structure.

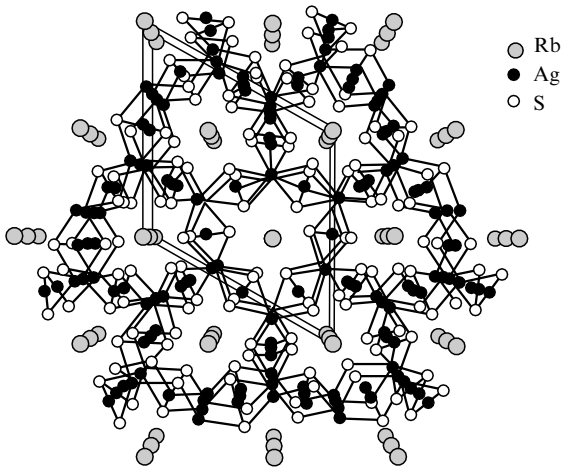


Figure 22. Projection of the structure of $RbAg_5S_3$ along the *c* axis;[108] columns containing Rb^+ ions are shown.

The structure of the cesium salt $CsAg_7S_4$ is unique. The crystals contain the eight-membered Ag_4S_4 rings in which the silver and sulfur atoms adopt the coordination numbers of 2 and 3, respectively. These rings, as in the structure of $RbAg_5S_3$, are linked to each other through the silver atoms, which have a nearly linear coordination. The $Ag^+ - Ag^+$ contacts, as in the rubidium salt, are in the range of 0.2961–0.3087 nm.[99] The rings are packed in infinite stacks. The channels (with a diameter of ~0.6 nm) formed in the structure are occupied by the cesium ions (Fig. 23).

Analysis of these structures allows the conclusion to be drawn about the similarity of the structural motifs of ternary copper and silver chalcogenides satisfying Zintl's concept. The ions with the d^{10} configuration have the linear or trigonal coordination, whereas the copper ions, which exist in a formal oxidation state greater than +1, are tetrahedrally coordinated.

The compounds of the series of chalcogenides of the general formula MB_3X_2 (M is alkali metal or thallium; B = Cu or Ag; X = S or Se) can be considered as chalcogenide derivatives MCu_2X_2

$$MCu_2X_2 + Cu \longrightarrow MCu_3X_2. \quad (5)$$

As in the case of reaction (1), the insertion of an additional copper atom leads to annihilation of holes in the valence band and causes the metal–semiconductor transition. Since the compounds of the MB_3X_2 series meet Zintl's criterion, *i.e.*, contain only B^+ ions, these compounds may be thought to possess a structural motif identical to that of the above-considered silver salts.

The first compounds of this series to be prepared by the carbonate procedure were the silver salts $RbAg_3S_2$ and $CsAg_3S_2$.[111] Their structures are isotypic and are in many respects similar to the structure of $K_2Ag_4S_3$. In both cases, the sulfur and silver atoms form layers between which the alkali metal atoms are

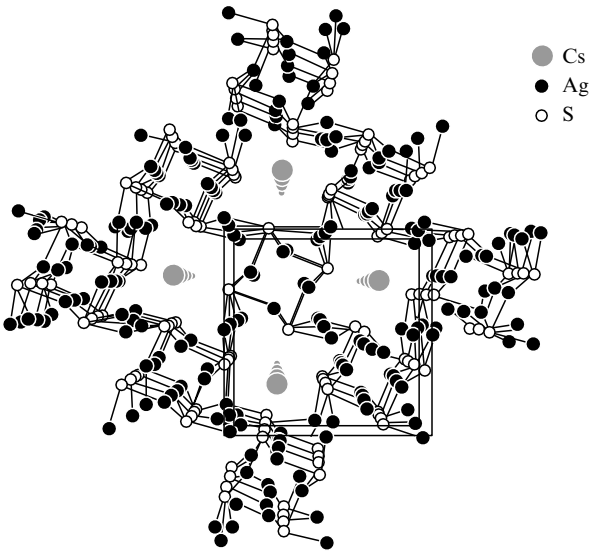


Figure 23. Projection of the structure of $CsAg_7S_4$ along the *c* axis;[108] channels formed by eight-membered rings are shown.

located, with the only difference that these layers in MAg_3S_2 are parallel to the (001) plane, whereas these layers in $K_2Ag_4S_3$ are parallel to the (100) plane (see Fig. 21 *a*, *b*). However, the structures of the layers are different. Thus in the structure of $K_2Ag_4S_3$, the eight-membered Ag_4S_4 rings are linked to each other *via* shared vertices through the bridging sulfur atoms, whereas the analogous rings in MAg_3S_2 are linked *via* shared edges. In Fig. 21 *a*, *b*, the fused Ag_4S_4 rings, which are similar in appearance but crystallographically nonequivalent, are hatched.

The first compound of the series of copper chalcogenides to be synthesised was sulfide KCu_3S_2, which was prepared by heating a mixture of K_2CO_3, copper and sulfur to 850 °C under an Ar atmosphere.[112] When the reaction was performed at a temperature lower than 780 °C, sulfides KCu_4S_3 and $K_3Cu_8S_6$ were obtained[99] (see below). The KCu_3S_2 salt exists as bright black needle-like crystals insoluble in water. These crystals as well as the crystals of MAg_3S_2 (M = Rb or Cs) belong to the same structural type (X-ray diffraction data).

Later on,[88] the cesium salt $CsCu_3S_2$ was prepared by the carbonate procedure. It was found that brief heating (up to 1.5 h) at 700 °C afforded $CsCu_4S_3$. However, an increase in the duration of annealing and in the temperature (4 h, 800 °C) resulted in the $CsCu_3S_2$ salt, which was free from admixtures. Unlike the blue-black crystals of $CsCu_4S_3$, the crystals of $CsCu_3S_2$ are transparent and almost colourless. Since these crystals are oxidised in air and develop a dark-brown colour, they are stored under an inert atmosphere. From the colour of the crystals and their composition, which satisfies Zintl's criterion, $CsCu_3S_2$ can be unambiguously assigned to compounds possessing dielectric properties.

In spite of the formal similarity to KCu_3S_2, the crystal structure of $CsCu_3S_2$ is quite different (the CdI_2 structural type). The sulfur atoms form hexagonal close packing. Half of octahedral positions are occupied by layers of Cs^+ ions. The layers with unoccupied octahedral positions, which remain unoccupied in the structure of CdI_2, are filled with copper atoms located at the centres of the edges of the octahedra (Fig. 24). The sulfur (the coordination number is 3) and copper (the coordination number is 2) atoms form layers perpendicular to the *c* axis. The copper ions have a linear coordination, which is uncommon in the chemistry of alkali chalcogenides of copper. It is evident from the above-considered examples of chalcogenides, which meet Zintl's criterion, that trigonal coordination or trigonal coordination combined with the linear coordination is more typical of these compounds.

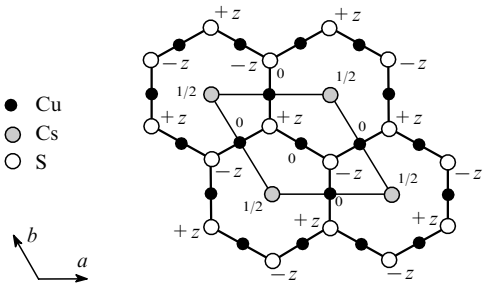


Figure 24. Projection of the structure of $CsCu_3S_2$ along the *c* axis.[88]

In the above-considered sulfide KCuS, the copper atoms have a linear coordination (the SCuS angle is 179°). However, the crystal structure consists only of chains, which impart the quasi-one-dimensional structure to this salt. The Cu–S distances in KCuS (0.213 and 0.216 nm) and in $CsCu_3S_2$ (0.217 nm) are virtually identical and are typical of copper sulfides with covalent bonds.

The thallium chalcogenides $TlCu_3X_2$ (X = S or Se) described previously[85,113–117] were synthesised in two stages. Initially, Tl_4S_3 was prepared from the elements. Then, the fusion of the latter with copper and sulfur afforded sulfide $TlCu_3S_2$.

These chalcogenides are very sensitive to oxidising agents. Thus, the selenide is oxidised in air, whereas active oxygen formed upon decomposition of hydrogen peroxide is required to oxidise the sulfide. The reaction

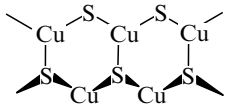
$$TlCu_3X_2 \longrightarrow TlCu_2X_2 + Cu \qquad (6)$$

can be performed by oxidation (including electrochemical oxidation[116,117]). Berger called this reaction 'extraction' of copper from $TlCu_3X_2$. This reaction is analogous to the above-described process (1) for the KCu_5S_3–KCu_4S_3 system and can be formally represented by Scheme (5). To perform chemical oxidation, powdered $TlCu_3S_2$ was deposited on a glass filter (with the aim of performing the process in a dynamic mode) and an ammonia solution of hydrogen peroxide, which decomposed under the action of the sulfide, was added dropwise. Ammonia that was released coordinated the Cu^{2+} ions, which were formed as result of oxidation, thus facilitating their extraction into a solution.

Selenide KCu_3Se_2 was synthesised by heating (910 °C, 3 h) a mixture of powdered copper, potassium and copper selenide in a quartz tube.[118] The KCu_3Se_2 salt was obtained as well-faceted black platelet-like crystals. Its crystal structure is analogous to that of $TlCu_3Se_2$ (X-ray diffraction data).

The data on other copper selenides MCu_3Se_2 are unavailable in the literature. However, analogous silver selenides $RbAg_3Se_2$ and $CsAg_3Se_2$ were reported.[109] Both salts crystallise as dark anthracite-like crystals and are readily oxidised in air. Their structures are similar to those of the analogous sulfides. The selenium and silver atoms form layers separated by layers of the M^+ ions.

Sulfide $Na_2Cu_3S_3$, which crystallised as needles, was described in a pioneering study.[99] More recently, it was demonstrated[119] that this sulfide has in fact the composition $Na_3Cu_4S_4$ and its structure contains the $[Cu_4S_4]_n^{3n-}$ stacks. Below is schematically shown the formation of these stacks from the *cis*-CuS chains. The coordination about the copper atoms is planar-trigonal.



The stacks are separated by the Na^+ ions, thus imparting the quasi-one-dimensional electronic structure to the crystals. The shortest Cu–Cu distances (0.2619–0.306 nm) satisfy Goodenough's criterion. Besides, the $Na_3Cu_4S_4$ salt is a mixed-valence compound. As was noted in the study,[119] all copper atoms in the

structure are equivalent, which is typical of metallic bonds (electrons delocalised along the $[Cu_4S_4]_n^{3n-}$ stacks), and sulfide $Na_3Cu_4S_4$ should exhibit metallic properties.

The electrophysical properties of this sulfide were examined.[100, 120] The electrical resistance of single crystals of $Na_3Cu_4S_4$ was found [120] to change linearly as the temperature decreased over the range from 300 to 150 K. Below 150 K, the $\rho(T)$ dependence becomes weaker, tends to saturation and reaches 3.3×10^{-6} Ω cm at 15 K.[100]

The electrical resistances for tableted samples at 293 K ($\rho_{RT} = 3.3 \times 10^{-3}$ Ω cm) and 15 K ($\rho_{15} = 6.7 \times 10^{-4}$ Ω cm) were reported.[100] For single crystals, the electrical resistance along the crystal axis, *i.e.*, along the stacks, was measured ($\rho_{RT} = 6.5 \times 10^{-5}$ Ω cm). This $\rho(T)$ dependence is characteristic of metals.

Although Ghosh and Chaudhury [100] failed to measure $\rho_\perp$ (the resistance perpendicular to the stacks), the noticeable difference (by a factor of ~ 50) in the resistance of tableted samples and single crystals is indicative of the substantial anisotropy of the electrical resistance. The temperature-independent paramagnetism, which was found in the studies [100, 120] (150×10^{-6} and 170×10^{-6} emu mol^{-1}, respectively), is also evidence in favour of the metallic state of $Na_3Cu_4S_4$.

It should be noted that the change in the specific electrical resistance according to the law

$$\rho = \rho_0 + \rho' T \qquad (7)$$

is typical of normal metals, unlike quasi-one-dimensional molecular metals, whose specific resistance changes quadratically. The authors [100, 120] used the approach proposed by Jellinek in studies of sulfide $Na_3Cu_4S_4$ as a salt containing only Cu^+ ions and mentioned that the oxidation state of +2 for copper atoms was not revealed by X-ray photoelectron spectroscopy. Curiously, the authors [120] considered all sulfur atoms as being also identical, whereas Jellinek's concept requires the presence of S^{2-} and S^- ions in the structure. However, this is quite reasonable when it is considered that the compound under study is a metal and the electrons are delocalised along the stacks. In this case, the valence fluctuations $Cu^{2+} \rightarrow Cu^+$ within the stack occurred in $\sim 10^{-16}$ s.

The absence of the metal–nonmetal transition up to 13 K and the peculiarities in the $\rho(T)$ dependence associated with the formation of charge density waves (CDWs) are not understood. It is known [121] that the so-called Peierls instability, which is manifested in the structural distortion of the one-dimensional chain associated with the increase in its period, is characteristic of quasi-one-dimensional metals. If the degree of filling of the band with electrons or holes is n^{-1}, a decrease in the temperature leads to *n*-merisation of the chain accompanied by splitting of the conduction band in such a way that the metal–nonmetal transition occurs. In this case, the larger is *n*, the smaller the gain in energy.

The reasons for the absence of the Peierls transition in the crystals of $Na_3Cu_4S_4$ up to 13 K were theoretically examined.[122] In particular, it was noted that $Na_3Cu_4S_4$ is a one-dimensional metal because the shortest distance between the adjacent one-dimensional $[Cu_4S_4]_n^{3n-}$ stacks (0.423 nm) in this salt is substantially larger that the sum of the van der Walls radii of sulfur atoms (0.360 nm). Calculations within the framework of the extended Hückel method demonstrated that the Fermi level intersects two bands, each being formed half by the 3*d* orbitals of the copper atoms and half by the 3*p* orbitals of the sulfur atoms. Hence, Whangbo and Canadell [122] believed that the hybrid formula including both the Cu^{2+} and S^- ions, *viz.*, $Cu_3^+Cu^{2+}S_4^{2-}$ and $Cu_4^+S_3^{2-}S^-$, is more adequate than Jellinek's formalism. This view is similar to our approach to the interpretation of the electronic structures of copper chalcogenides, which do not meet Zintl's concept.

Whangbo and Canadell [122] believed that the state with CDWs preceding the Peierls transition is not formed due, probably, to the fact that the stabilisation of the electronic energy is exactly compensated by the deformation energy of the stack. In the case of one-dimensional metals in the absence of states with CDWs, an alternative possibility consists in the formation of spin density waves (SDWs), which is generally observed at lower temperatures. In a review,[121] we noted that the spin–lattice interaction responsible for the spin-Peierls transition is more efficient than the electron–lattice interaction at $t \approx U$, where t is the integral of the electron transition between the nearest electronic states and U is the interaction energy of two electrons located at one node. In one-dimensional conductors $[MS_4C_4(CF_3)_4]$TTF (M = Cu or Au; TTF is tetrathiafulvalene), the spin-Peierls transition is observed at 12 (Cu) and 2.1 K (Au). I believe that the deviation of the $\rho(T)$ dependence from the linearity for $Na_3Cu_4S_4$ at $T < 80$ K is, probably, caused by fluctuations preceding the spin-Peierls transition at $T < 13$ K.

A series of ternary copper sulfides M_nCuS with the Cu : S ratio of 1 : 1 can be distinguished based on formal attributes. In this series, all members with *n* from 0 (CuS) to 1 (KCuS) are known, the *n* value varying with a step of 0.25. Thus, the above-considered sulfide $Na_3Cu_4S_4$ corresponds to $n = 0.75$, whereas the above-considered layered sulfides MCu_2S_2 (the first members of the $MCu_{2n}X_{n+1}$ series) are characterised by $n = 0.5$. Finally, sulfide $NaCu_4S_4$ synthesised in 1996 [123] corresponds to $n = 0.25$. It should be noted that the M_nCuS series can be distinguished only formally because the insertion of alkali metal into the lattice of CuS leads not only to a change in the electronic properties but also to a change in the structure. Thus, unlike $Na_3Cu_4S_4$, which has a quasi-one-dimensional stack structure, $NaCu_4S_4$ has a layered structure, though formally contains the same Cu_4S_4 structural elements.

Heating of a mixture of copper, Na_2S and BaS with sulfur (taken in a ratio of 1 : 3 : 0.5 : 6, respectively) in an evacuated glass tube (500 °C, 4 days) followed by cooling at a rate of 4 °C/h afforded a melt, which was freed off from polysulfides with water and DMF under a nitrogen atmosphere. As a result, platelet-like black crystals of $NaCu_4S_4$ were obtained in 79% yield.

The crystals consist of trigonal-symmetrical layers of CuS alternating with layers of Na^+ ions (Fig. 25). The structure of $Na_{0.25}CuS$, like CuS, contains both sulfide and disulfide ions. The $[Cu_4S_2(S)_2]^-$ layers have the sandwich structure: the Cu_2S_2 layers (the *anti*-GaS structural type) are located between two CuS layers (the BN structural type). These layers are linked through the copper atoms from the *anti*-GaS layer and through the sulfur atoms from the BN layer to form the Cu–S bond resulting in four-coordinate S^{2-} ions with the unusual inverted tetrahedral geometry. Unlike the structurally similar CuS salt in which the Cu_2S_2 layers of the *anti*-GaS type alternate with the CuS layers of the BN type, half of the *anti*-GaS layers in $NaCu_4S_4$ are replaced by layers of Na^+ ions. Therefore, the structure of $NaCu_4S_4$ contains two crystallographically nonequivalent copper atoms,

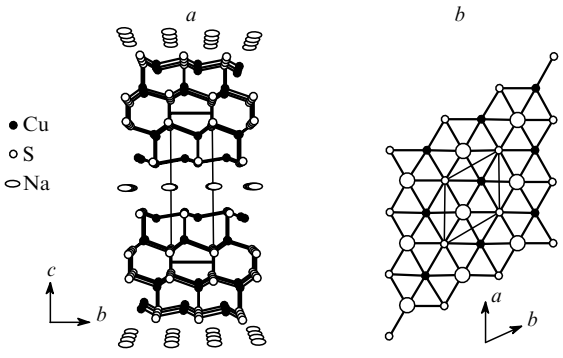


Figure 25. Packings of the atoms in $NaCu_4S_4$ (*a*) and in the $[Cu_4S_4]^-$ ions (*b*) along the *c* axis (large and small empty circles denote S atoms from two different layers).

viz., the copper atom tetrahedrally coordinated by one S^{2-} ion and three S_2^{2-} ions and the trigonally coordinated copper atom.

Sulfide $NaCu_4S_4$ is a metal with the hole conductivity. Its electrical resistance increases linearly with temperature in the range from 4.2 to 250 K. From measurements of the thermoelectromotive force it follows that holes act as charge carriers. This salt possesses the Pauli paramagnetism, $\chi_M = 6.2 \times 10^{-5}$ emu mol^{-1}.

Sulfide $BaCuS_3$, which we prepared [124] by heating a mixture of BaS, CuS and sulfur taken in stoichiometric amounts (800 °C, 2 h), has no analogues. This sulfide was formed as black bright platelet-like crystals belonging to the monoclinic system. Since the composition of this sulfide does not satisfy Zintl's criterion, it is believed that this compound is a metal. Actually, the specific resistance ($\rho_{RT} = 9.4 \times 10^{-2}$ Ω cm) of the samples, though large, decreases as the temperature decreases and reaches 0.037 Ω cm at 15 K. Unlike other ternary copper sulfides, the $\rho(T)$ dependence is described by a fractional-rational rather than by a linear function

$$\rho(T) = \frac{1 + \alpha T}{\beta + \gamma T}, \tag{8}$$

where $\beta^{-1} = \rho(0)$, *i.e*., $\beta = \sigma(0)$, $\alpha/\gamma = \rho(\infty)$.

Equation (8) can be rewritten in a more customary form

$$\rho(T) = \rho_\infty + \frac{a}{b + T} \tag{9}$$

with the 'Curie-like' second term. The magnetic susceptibility of metals containing paramagnetic centres is described by this formula. In the case of $BaCuS_3$, the following parameters were obtained for Eqn (9): $\rho_\infty = 0.136$ Ω cm, $a = -18.98$ Ω cm K^{-1} and $b = 178.3$ K.

Note that the temperature dependence of the electrical resistance described by Eqn (9) is untypical of all conducting materials, and not just of ternary sulfides. Analysis of the published data makes it possible to reveal analogous $\rho(T)$ dependences for $Cu_{1.5}Co_{1.5}S_4$,[125] which has the spinel structure, for $Rb_4Mo_{18}Se_{20}$ [126] consisting of Mo_6Se_8 clusters and for spinel-like $CuRh_2S_4$ and $CuRh_2Se_4$.[127] The dependences reported in these studies are well described by Eqn (9). Apparently, the authors [127] failed to approximate the $\rho(T)$ dependence throughout the temperature range because the high-temperature region was described by the linear function (7), the temperature range with $T < 20$ K was described by the function

$$\rho(T) = \rho_0 + AT^n \tag{10}$$

with $n = 3$, whereas the temperature range from 20 to 250 K was not interpreted. The authors considered this dependence as the supporting evidence for the applicability of the Wilson model. However, the $\rho(T)$ dependence for single crystals of $BaCuS_3$ as well as that for chalcogenides studied in Refs 125–127 are described by Eqn (9) throughout the temperature range (from 300 K up to the superconducting transition). This result should give impetus to theoretical studies in the field of solid-state physics.

Sulfide $K_3Cu_8S_6$, which was the first representative of ternary copper chalcogenides of the general formula $M_3Cu_8X_6$ (M is alkali metal and X = S or Se), was synthesised as early as the mid-nineteenth century.[128] Later on, this sulfide, along with other salts described above, was prepared according to the carbonate procedure and studied by the X-ray diffraction method.[99] However, the structure of this compounds remained unknown. In 1979, structural studies demonstrated [129] that this sulfide as well as the rubidium analogue $Rb_3Cu_8S_6$ have layered structures analogous to that of KCu_3S_2. The structures of three sulfides, *viz*., KCu_3S_2 ($K_3Cu_9S_6$), $K_3Cu_8S_6$ and KCu_4S_3 ($K_2Cu_8S_6$), are shown in Fig. 26 *a*–c. This comparison, which is not just formal, confirms that $K_3Cu_8S_6$ is intermediate between sulfides KCu_3S_2 and KCu_4S_3. It was demonstrated [130] that KCu_4S_3 occurs as a low-temperature phase, which is stable up to 820 °C. At higher temperatures, the KCu_3S_2 phase is stable. Sulfide $K_3Cu_8S_6$ occurs as a metastable phase. The optimum conditions for the synthesis of the latter consist in annealing at 875 °C for 1–2 h.

As can be seen from Fig. 26 *a*, the low-temperature KCu_4S_3 phase contains close-packed layers in which all copper atoms are tetrahedrally coordinated. In the high-temperature KCu_3S_2 phase (Fig. 26 *c*), the layers are corrugated because the copper atoms adopt both the tetrahedral and trigonal coordinations. The structure of $K_3Cu_8S_6$ is intermediate between the above-described structures. The $[Cu_4S_4]_n^{n-}$ chains are linked in layers *via* shared edges of the tetrahedra so that the semisegment of the double layer, which is observed in KCu_4S_3, is formed. The $Rb_3Cu_8S_6$ salt has the analogous structure.[129]

In the same year, selenides $Rb_3Cu_8Se_6$ and $Cs_3Cu_8Se_6$ were synthesised by the carbonate procedure from powdered copper and selenium sulfide.[131] After annealing at 900–1050 °C (3–4 h), the melt was slowly cooled and washed with water and alcohol to obtain dark anthracite-like crystals. The structure of $Rb_3Cu_8Se_6$ is similar to those of sulfides $K_3Cu_8S_6$ and $Rb_3Cu_8S_6$. Apparently, the cesium salt crystallises in two modifications one of which is analogous to $Rb_3Cu_8Se_6$, whereas the second modification was not identified. The results of electrophysical measurements for selenides are unavailable in the literature. However, based on their compositions and on the shortest Cu–Cu distances (0.2488–0.2893 nm) in these compounds, it can be said with assurance that these compounds are metals.

The electrophysical and magnetic studies of the crystals of $K_3Cu_8S_6$ were performed.[130] The magnetic susceptibility depends only slightly on the temperature at $T > 180$ K. However, this dependence becomes pronounced at temperatures lower than 180 K, which is indicative of a phase transition of the second kind. This transition is reversible. The transition temperature can be determined more accurately from the temperature dependence of the $(\partial\chi/\partial T)$ derivative (150 K). At approximately 50 K, the second transition (of the first kind) with the noticeable hysteresis was observed.

The electrical resistance of single crystals of $K_3Cu_8S_6$ is 5×10^{-4} Ω cm; the $\rho(T)$ dependence was measured in the range of 350–5 K.[131] The resistance decreases linearly as the temperature decreases, which is indicative of the metallic behaviour of

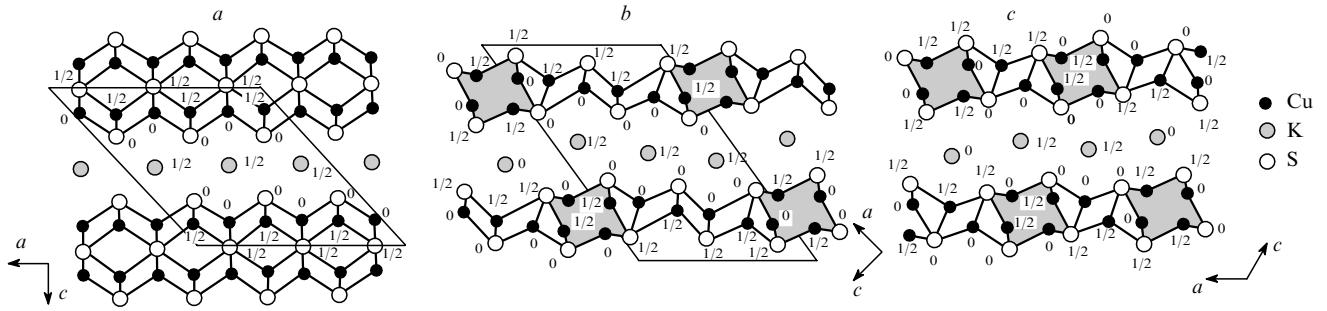


Figure 26. Structures of sulfides KCu_4S_3 (*a*), $K_3Cu_8S_6$ (*b*) and KCu_3S_2 (*c*).[130] In all the structures, the K^+ ions separate layers.

single crystals of $K_3Cu_8S_6$ down to 160 K. At about 150 K, a reversible phase transition occurs, which is manifested in an increase in the resistance in the course of subsequent cooling to 63 K. At this temperature, the resistance decreases sharply and from this point on the $\rho(T)$ dependence again corresponds to the metallic behaviour in the region of 50 – 5 K. The anomaly at about 160 K is also present in the temperature dependence of the thermoelectromotive force. Its plus sign confirms that $K_3Cu_8S_6$ is a metal with hole conductivity. In a study,[131] all these anomalies were attributed to the occurrence of the state with CDWs, which is typical of low-dimensional metals, *viz*., of quasi-one-dimensional salts {for example, of $K_2[Pt(CN)_4]Cl_{0.3}\cdot xH_2O$ and $NbSe_3$} and of quasi-two-dimensional salts ($TaSe_2$). However, this state can also occur in three-dimensional metals (for example, in CuV_2S_4). Sulfide $K_3Cu_8S_6$ can be considered (as is evident from its structure) as a quasi-two-dimensional metal. However, unlike quasi-two-dimensional metals, such as, for example, $NbSe_2$ or TaS_2, the layers in $K_3Cu_8S_6$ are noticeably anisotropic, as is evident from the mode of linkage of the Cu_4S_4 columns in layers. The fact that the metallic properties are retained at temperatures lower than the phase transition temperature indicates that this anisotropy is yet inadequate to consider the crystals of $K_3Cu_8S_6$ as quasi-one-dimensional. An analogous ansisotropy of the layers occurs, for example, in molybdenum bronze $K_{0.3}MoO_3$, which is a structurally two-dimensional metal with a essentially monomeric CDWs.

X-Ray scattering was studied at different temperatures [132] and it was found that the phase transition at 153 K generates states, which are incommensurate with the lattice period, with the wave vector

$$q = \frac{(1-\delta)b^*}{2},$$

where δ is the temperature-dependent variable ($\delta \approx 0.1$ at 150 K) and b^* is the reciprocal lattice vector. At 55 K, the wave vector of CDW becomes commensurate with the lattice period, which leads to a structural phase transition resulting in the superstructure with the commensurate period at $q = (\frac{1}{2}, \frac{1}{2}, 0)$. Sulfide $K_3Cu_8S_6$ is the first example of a metal with the hole conductivity in which CDWs with pronounced *p* character appear.

In conclusion, let us consider a few available examples of tellurides of Group IB elements containing discrete Te^{2-} or Te_2^{2-} ions.

Thus, ternary copper tellurides with compositions MCuTe [97] and MCu_3Te_2 [104, 133] (M = Na or K) satisfying Zintl's criterion were described. In 1976, telluride $TlCu_2Te_2$ was synthesised from the elements (600 °C, 48 h).[134] This telluride can be assigned to the series of $MCu_{2n}X_{n+1}$ chalcogenides. According to the data of X-ray diffraction analysis, this telluride is isostructural to selenide $TlCu_2Se_2$. The electrophysical properties of the telluride under consideration were studied in Ref. 90. The electrical resistance (293 K) of single crystals of $TlCu_2Te_2$ is 2.3×10^{-5} Ω cm. The $\rho(T)$ dependence is analogous to that corresponding to metals, *viz*., the resistance decreases linearly (by a factor of 3.5) as the temperature decreases and reaches 6.5×10^{-6} Ω cm at 77 K. Holes act as charge carriers (the results of measurements of the Hall effect). Although the electrical resistance decreases as the samples are cooled, the ρ_{300}/ρ_{77} ratio is rather small. This is attributable to the fact that the concentration of the carriers in the sample decreases substantially (by a factor of 21) in the range of 300 – 77 K simultaneously with an increase (by a factor of 76) in the carrier mobility (from 34 $cm^2\ V^{-1}$ at 300 K to 2600 $cm^2\ V^{-1}$ at 77 K), *i.e*., the effect of an increase in the carrier mobility is more pronounced than the effect of a decrease in their concentration. This leads to an increase in the conductivity upon cooling. To put it differently, $TlCu_2Te_2$ would be more properly characterised as a semimetal.

Layered mixed-valence telluride $K_2Cu_5Te_5$ was synthesised [135] by heating the telluride K_2Te with copper and tellurium in an evacuated tube (350 °C, 3 days). The telluride was obtained as black parallelepiped-shaped crystals. The structure of this salt consists of the corrugated $[Cu_5Te_5]_n^{2n-}$ layers alternating with the layers of the potassium ions. The $[Cu_5Te_5]_n^{2n-}$ layers are formed by the Cu_2Te_2 rhombi linked *via* shared edges so that their structure corresponds to the distorted *anti*-PbO type. A comparison with the structure of CuTe demonstrates that the addition of 0.4 e per CuTe molecule leads to the cleavage of some of Te – Te bonds in $K_2Cu_5Te_5$, whereas the addition of one electron (as in NaCuTe) leads to the cleavage of all Te – Te bonds and generates the ideal structure of the *anti*-PbO type. Therefore, $K_2Cu_5Te_5$ is intermediate between CuTe and NaCuTe.

The electrical resistance and the thermoelectromotive force were measured for $K_2Cu_5Te_5$ and it was revealed that this telluride is a *p*-type metal in the range of 300 – 5 K. The electrical resistance is 6.67×10^{-5} Ω cm at 293 K and reaches 3.1×10^{-6} Ω cm at 5 K. The telluride possesses temperature-independent paramagnetism (2.56×10^{-4} emu mol^{-1}).[135]

The electronic structure of the $K_2Cu_5Te_5$ salt was studied by quantum-chemical calculations using the extended Hückel method.[136] Since the conductivity increases only insignificantly as the temperature decreases in the range of 293 – 5 K, the nature of the ground state remains unclear, *i.e*., the question of whether this telluride is a metal or a semimetal remains open. Another problem studied in Ref. 136 is associated with the possibility of the synthesis of tellurides $K_3Cu_5Te_5$ and KCu_5Te_5. In particular, the question was studied of whether the addition of one electron to the $[Cu_5Te_5]^{2-}$ layer or removal of one electron from this layer can lead to the metal – nonmetal transition.

According to the data obtained, the pre-Fermi region ($\varepsilon_F = -10.5$ eV) from −10.1 to −12.6 eV is formed predominantly by the 5*p* orbitals of tellurium atoms, whereas the region from −12.6 to −16 eV is formed by the 3*d* orbitals of copper atoms. A broad gap extends from −10.1 to −7.5 eV. However, a narrow peak corresponding to σ* antibonding orbitals of the Te(2) – Te(2) bond is present at −8.3 eV (Fig. 27). The scheme of the structure of the $[Cu_5Te_5]_n^{2n-}$ layer is shown in Fig. 27. It can be seen that this layer contains three types of tellurium atoms. Only the Te(2) atoms are involved in formation of the Te – Te bonds. The populations of the $5p_y$ states of the tellurium atoms are approximately equal [1.43, 1.45 and 1.49 e for Te(1), Te(2) and Te(3), respectively], *i.e*., holes are to a large extent delocalised in the layer. This fact as well as the approximately equal Cu(2) – Te(1) and Cu(3) – Te(3) distances allows one to consider $K_2Cu_5Te_5$ as a metal. From the results of calculations it follows that the crystals of this telluride should exhibit the noticeable anisotropic conductivity. Unfortunately, it was impossible to measure this anisotropy because of small dimensions of the crystals.

The addition of one electron to the $[Cu_5Te_5]_n^{2n-}$ layer, which corresponds to the tranformation to $K_3Cu_5Te_5$, leads to filling of the *p* band formed by the 5*p* orbitals of the tellurium atoms. One would expect that this will result in the metal – nonmetal transition. However, it was demonstrated [136] that the insertion of potassium leads not only to an increase in the degree of filling of the *p* band but also to structural changes. The structure of $K_2Cu_5Te_5$ contains vacancies sufficient for location of potassium ions above the Te(2) – Te(2) bonds. The insertion of potassium leads to the cleavage of the bonds. In this case, the peak localised at −8.3 eV is broadened and merges with the *p* band. As a result, $K_3Cu_5Te_5$ retains the metallic properties, possesses two holes per formula unit and is a structural analogue of the NaCuTe salt.

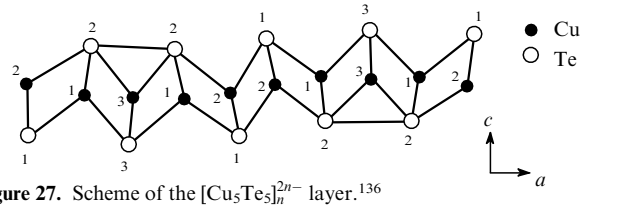


Figure 27. Scheme of the $[Cu_5Te_5]_n^{2n-}$ layer.[136]

Upon the removal of one electron, which corresponds to the transformation to KCu_5Te_5, the Te(1)–Te(3) bond could be formed, *i.e.*, the Te_2^{2-} ion could be formed if the potassium atoms located above this bond are removed. This would result in the formation of the energy gap, *i.e.*, in the metal–nonmetal transition. However, according to the results of the study,[136] the metallic state is retained in this case because there are three Te–Te bonds per two holes with respect to $K_2Cu_{10}Te_{10}$.

As part of continuing studies of reactions proceeding in melts of polytellurides, Zhang *et al.*[137] prepared a new class of polytellurides containing dodecahedral $[Cu_8Te_{12}]$ clusters, *viz.*, $K_4Cu_8Te_{11}$, $M_3Cu_8Te_{10}$ (M = Rb or Cs), $M,M'_2Cu_8Te_{10}$ (M, M′ = K, Rb or Cs) and $M_2BaCu_8Te_{10}$ (M = K, Rb or Cs). Telluride $K_4Cu_8Te_{11}$ has a three-dimensional framework structure formed by the $[Cu_8Te_{12}]$ clusters linked to each other. Each layer contains an encapsulated K^+ ion (Fig. 28). The structure contains channels parallel to the *b* axis. These channels are occupied by potassium ions. The $[KCu_8Te_{12}]^{3-}$ clusters are ideal platon bodies (the point symmetry group T_h) formed by the Cu_2Te_3 planar pentagons linked to each other. Each tellurium atom belongs to a Te_2^{2-} ion so that the clusters are in fact formed by the copper and ditelluride ions $[Cu_8(Te_2)_6]$.

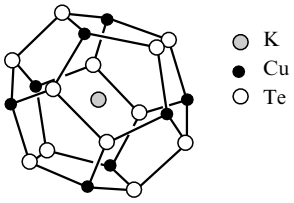


Figure 28. Structure of the $[Cu_8Te_{12}]$ cluster inside which the K^+ ion is located.[137]

Unlike the $K_4Cu_8Te_{11}$ salt containing three-dimensional networks of the clusters, the $Rb_3Cu_8Te_{10}$ and $Cs_3Cu_8Te_{10}$ compounds have layered structures. The $Rb_3Cu_8Te_{10}$ salt consists of $[RbCu_8Te_{10}]_n^{2n-}$ layers alternating with the layers of Rb^+ ions. In spite of a substantial structural difference, the major structural blocks in the latter salt are identical to those observed in $K_4Cu_8Te_{11}$. The layers are formed by the $[Cu_8Te_{12}]$ pentagonal dodecahedra linked to each other. The Rb^+ ions are encapsulated into these layers. The structure of the cesium salt is analogous to that of the rubidium salt.

The structural studies of the salts with the mixed composition demonstrated that incapsulation is favourable for ions of smaller radii. Thus, in the $KCs_2Cu_8Te_{10}$ and $KRb_2Cu_8Te_{10}$ salts, the potassium ions are located inside the dodecahedra.

The $K_2BaCu_8Te_{10}$ and $Rb_2BaCu_8Te_{10}$ salts are isomorphous with the $Rb_3Cu_8Te_{10}$ salt. The centre of the dodecahedral cavity is occupied by the Ba^{2+} ion, whose ionic radius is close to that of the K^+ ion. In the case of the potassium salt, the K^+ ions are located between the layers, which implies that encapsulation of the ion with the larger charge is more favourable in the case of the equal ionic radii.

Zhang *et al.*[137] studied the electrophysical and optical properties of the tellurides synthesised. According to the structural data, the formula of the $K_4Cu_8Te_{11}$ salt can be written as $K_4Cu_8(Te_2)_5Te$. Taking the charges of the ditelluride and telluride ions to be equal to −2 and the charge of the copper ions to be equal to +1, it can be concluded that this salt satisfies Zintl's criterion and, consequently, should exhibit semiconducting properties. This suggestion is also confirmed by the fact that the electrical resistance of the crystals of $K_4Cu_8Te_{11}$ (293 K) is rather small (6.25×10^{-3} Ω cm) but it increases according to the activation law as the temperature decreases.

The $M_3Cu_8Te_{10}$ and $MM'_2Cu_8Te_{10}$ salts (which do not meet Zintl's criterion) contain the $[Cu_8(Te_2)_4Te_2]^{3-}$ anions and, consequently, these salts are mixed-valence compounds. According to the results of quantum-chemical calculations,[137] the degree of oxidation of copper in these compounds is equal to +1 (the 3*d* orbitals of the copper atoms are located substantially lower than the 5*p* orbitals of the tellurium atoms). Therefore, the *p* band formed by the orbitals of the tellurium atoms contains one hole per formula unit. It is believed that these salts exhibit metallic properties. The data of electrophysical measurements confirmed that the $Rb_3Cu_8Te_{10}$, $Cs_3Cu_8Te_{10}$ and $KRb_2Cu_8Te_{10}$ salts exhibit metallic properties in the range of 5–300 K. Thus, the specific resistance of the samples of $Cs_3Cu_8Te_{10}$ decreases by almost three orders of magnitude from 1.1×10^{-3} Ω cm at 293 K to 1.2×10^{-6} Ω cm at 5 K. The ρ_5 value for this salt is the smallest among all chalcogenides based on copper.

The thermoelectromotive forces of the $M_3Cu_8Te_{10}$ salts are positive and increase linearly with temperature in the range of 90–300 K, which indicates that these compounds are metals with hole conductivity. The magnetic properties of these salts are also typical of metals. These salts exhibit temperature-independent paramagnetism.

The $M_2BaCu_8Te_{10}$ salts satisfying Zintl's criterion should be analogous to $K_4Cu_8Te_{11}$. It was found that $K_2BaCu_8Te_{10}$ and $Rb_2BaCu_8Te_{10}$ possess the low electrical resistances at 293 K. Their resistances increase only slightly as the temperature decreases down to ~ 150 K. Below 150 K, the electrical resistance increases more rapidly. This means that either these salts are degenerate semiconductors or they have a very narrow forbidden band. The optical measurements in the visible and UV regions revealed no gaps. However, the gap is observed in the IR region and it corresponds to 0.1 eV for the $Rb_2BaCu_8Te_{10}$ salt. The barium salts exhibit the temperature-independent paramagnetism typical of dielectrics.

The scarce data on copper tellurides allow one to make definite conclusions. Thus, the Te···Te contacts, which are shortened compared to the sum of the van der Walls radii, were found in tellurides $Na_6Te(Te_5)$, Na_2Te_6, M_2Te_3 (M = K, Rb or Cs), M_2Te_5 (M = Rb or Cs) and $CsTe_4$.[138] However, these contacts are absent in tellurides containing bulky cations, for example, in $(Ph_4P)_2Te_4 \cdot 2MeOH$ and Me_4NMTe_4 (M = Cu or Ag). Apparently, cations characterised by a high charge to radius ratio assist in decreasing Coulomb repulsions between polytelluride ions and in reducing the possibility of Te···Te interactions. In this connection, melts of polytellurides containing barium ions along with alkali metal cations were studied further. Thus, isomorphous polytellurides $NaBa_6Cu_3Te_{14}$ and $(K_{0.60}Ba_{0.40}).Ba_6Cu_{2.58}Te_{14}$ were isolated.[138] The structure of the $NaBa_6Cu_3Te_{14}$ salt is based on the $[Cu_3Te_3(Te_3)_3]^{9-}$ clusters of a new type. These clusters are six-membered rings formed by three copper atoms and three tellurium atoms. Each copper atom is coordinated in a bidentate fashion to the Te_3^{2-} ion, thus acquiring trigonal coordination (Fig. 29). Hence, the cluster ions each contain one six-membered ring and three four-membered rings. The $[Cu_3Te_3(Te_3)_3]^{9-}$ clusters are packed in stacks. The Na^+ ions are encapsulated into the cavities between these stacks. The composition of the stacks can be represented by the formula $[NaCu_3Te_3(Te_3)_3]_n^{8n-}$. Each stack is surrounded by six stacks formed by the Ba^{2+} ions. Each telluride ion is surrounded by six Ba^{2+} ions, thus adopting a trigonal-prismatic coordination environment. Therefore, the structure of this telluride is best described by the formula $Ba_6[NaCu_3Te_3(Te_3)_3]Te_2$, which satisfies Zintl's criterion. Because of this and taking into account the existence of ionic Te···Te contacts, which are shortened compared to the sum of the van der Waals radii, this telluride would be expected to be a narrow-band semiconductor or a semimetal.

This conclusion was confirmed by both electrophysical and optical measurements. Thus, ρ_{RT} is ~ 10 Ω cm, increases according to the activation law as the temperature decreases and reaches 2.5×10^3 Ω cm at 20 K, which corresponds to the width of the forbidden band of about 0.01 eV and to the absorption in the far-IR region (at about 40 cm^{-1}). According to the data of measure-

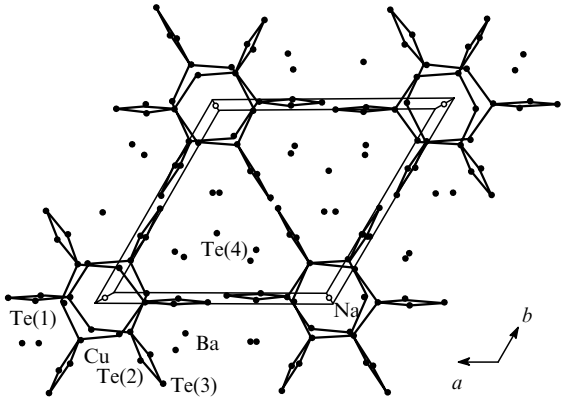


Figure 29. Packing of $NaBa_6Cu_3Te_{14}$ along the *c* axis.

ments of the thermoelectromotive force, telluride $NaBa_6Cu_3Te_{14}$ is a *p*-type semimetal (the Seebeck coefficient is ~ 100 μV K^{-1}).

The structure of telluride $(K_{0.60}Ba_{0.40})Ba_6Cu_{2.58}Te_{14}$ is very similar to that described above, with the difference that the cavities in the $[Cu_3Te_3(Te_3)_3]^{9-}$ stacks are statistically occupied by the K^+ and Ba^{2+} ions. The retention of the electroneutrality is provided by the presence of an equivalent number of vacancies in positions occupied by the copper atoms. This telluride is a *p*-type semiconductor. Its ρ_{RT} is 10^5 Ω cm, increases as the temperature decreases and reaches 10^{12} Ω cm at 130 K, which corresponds to the width of the forbidden band of 0.69 eV. Both tellurides possess diamagnetic properties.

Telluride $K_{0.33}Ba_{0.67}AgTe_2$ was described.[139] Unlike analogous tellurides based on copper, this telluride has a layered structure (Fig. 30), which is characterised by the presence of two type of monolayers separated by the K^+ and Ba^{2+} ions. One of the monolayers is a corrugated $[Ag_2Te_2]^{2-}$ layer and the second monolayer is a planar-square layer formed by the tellurium atoms. The degree of oxidation of the tellurium ions in the $[Te_2]^{4/3-}$ monolayer is $-2/3$ on the assumption that the degrees of oxidation of the silver and tellurium ions in the $[Ag_2Te_2]^{2-}$ layer are $+1$ and -2, respectively.

It should be noted that the existence of the ideal planar-square layers formed only by the tellurium atoms is the unique peculiarity of telluride $KBa_2[Ag_3Te_3]Te_3$. The crystals of the $RbTe_6$ and Cs_3Te_{22} salts[140] also contain planar layers of tellurium atoms. However, these layers can be considered as derivatives of the structure shown in Fig. 30 in which 2/5 of all tellurium atoms are removed. The double planar layers of tellurium atoms were found in the unusual $(Te_2)_2(I_2)$ compound,[141] which can be considered as a product of intercalation of tellurium by iodine.

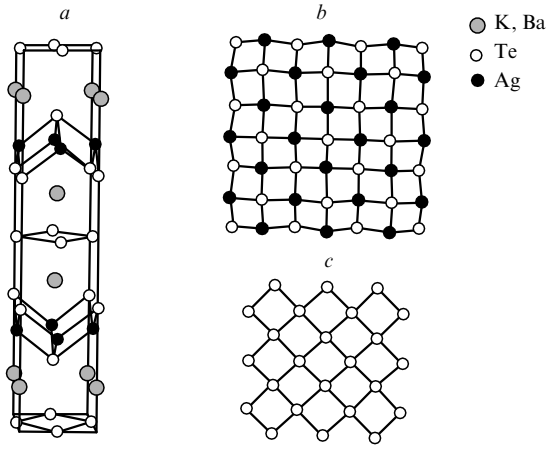


Figure 30. Structure of $K_{0.33}Ba_{0.67}AgTe_2$; (*a*) the unit cell; (*b*) the $[Ag_2Te_2]_n^{2n-}$ layers; (*c*) the $[Te_2]_n^{4n-/3}$ layers.[139]

The covalent interactions between the $[Ag_2Te_2]$ and $[Te_2]$ layers are negligible. According to the quantum-chemical calculations within the framework of the extended Hückel method, the Fermi level is located within the band formed by atomic orbitals of the tellurium atoms of the $[Te_2]$ layer. This corresponds to a gap in the band structure of the $[Ag_2Te_2]$ layers. Consequently, this compound can exhibit metallic properties due to the planar-square $[Te_2]$ layers.

The measurements of the electrical resistance and the thermoelectromotive force demonstrated that this telluride exhibits semiconducting properties. Thus, ρ_{RT} is ~ 5 Ω cm and increases according to the activation law as the temperature decreases. The width of the forbidden band, which was determined from the temperature dependence of ρ, is 0.06 eV to which the optical absorption at energies lower than 0.15 eV corresponds. The semiconducting properties of $K_{0.33}Ba_{0.67}AgTe_2$ are also confirmed by the results of measurements of the thermoelectromotive force. It has a positive value and the Seebeck coefficient is $200-300$ μV K^{-1}.

This discrepancy between theory and experiment may be accounted for by different reasons. Thus, it is quite apparent that nonrelativistic calculations for a salt containing the heavy atom, such as tellurium, are inadequate. Another possible reason is that the mixed-valence state of the silver ions in the telluride is absent because silver, unlike copper, obviously cannot exist in chalcogenides in the form of Ag^{2+}. The structural distortion of the $[Te_2]^{4/3-}$ layers due to the appearance of CDWs may be also responsible for the manifestation of semiconducting properties. The latter possibility was considered in Ref. 139. Since X-ray diffraction studies did not reveal structural distortions resulting in the deviation from the ideal I_4/mmm symmetry, the authors used the electron diffraction method, which is more sensitive to weak structural distortions of the $[Te_2]^{4/3-}$ layers. The electron diffraction data are unambiguously indicative of the presence of two superlattices. In one type of domain, distortions generate an incommensurate superlattice with $a^*_{super} = 0.352a^*_{sub}$; $b^*_{super} = b^*_{sub}$, $c^*_{super} = c^*_{sub}$. The domains of the second type contain a commensurate superstructure with $a_{super} = 3a_{sub}$; $b_{super} = 3b_{sub}$, $c_{super} = c_{sub}$. The results obtained confirm the suggestion that CDWs are responsible for localisation of electrons in the $[Te_2]^{4/3-}$ layers. The formal charge of the tellurium ions in the layers is equal to $-2/3$. Hence, the appearance of CDWs is associated with the formation of the Te_3^{2-} ions in the $[Te_2]$ layers in the case of the occurrence of the superstructures 3×3 and 3×1 because the charge, which fluctuates in the ideal square lattice, is localised on going to the tritelluride ion.

However, the available data on mixed copper tellurides, while rather scarce, demonstrate that tellurides differ substantially from sulfides and selenides. Although simple tellurides with compositions identical to those of sulfides and selenides exist, the majority of tellurides have no analogues among the corresponding sulfides and selenides. The same is true for their structures. Thus, the structures of CuS and CuSe are identical, whereas the CuTe structure is quite different. Unlike the widespread copper polysulfides, examples of the presence of polytelluride ions in copper salts are few in number. Thus, the isostructural α-$KCuX_4$ and $M_3Cu_8X_6$ salts (X = S or Se) are known, whereas the corresponding tellurides do not exist. At the same time, there are no sulfide analogues of $K_2Cu_5Te_5$ or $K_4Cu_8Te_{11}$.

As was mentioned in Chapter III, attempts to prepare mixed sulfide–telluride copper complexes from a melt of $M_2S_xTe_{1-x}$ afforded salts containing sulfide and trithiotelluride ions. Later on, the $MM'TeS_3$ salts (M = K, Rb or Cs; M′ = Cu or Ag) containing only TeS_3^{2-} ions, *viz.*, $CsCuTeS_3$, α- and β-$KAgTeS_3$, $RbCuTeS_3$, $RbAgTeS_3$ and $CsAgTeS_3$, were isolated.[142] The last-mentioned four salts are quasi-two-dimensional and isomorphous. These salts contain the anionic $[M'TeS_3]_n^{n-}$ layers between which the alkali metal ions are located (Fig. 31). The Cu^+ ions are coordinated by four sulfur atoms of the TeS_3^{2-} ions, thus adopting a distorted tetrahedral coordination. Each TeS_3^{2-} ion acts as a

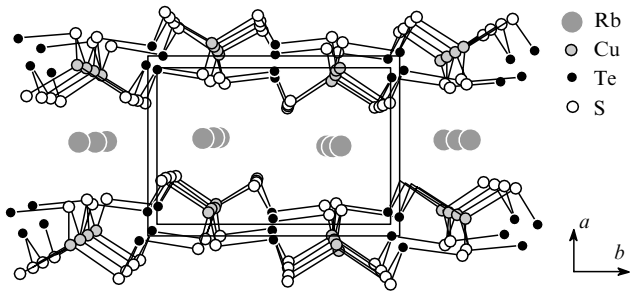


Figure 31. Two-dimensional structure of $RbCuTeS_3$ along the *c* axis. The rubidium ions form monoatomic layers between the $[CuTeS_3]_n^{n-}$ layers.[142]

bridge and links four Cu^+ ions. Two sulfur atoms each link one Cu^+ ion and the third sulfur atom acts as a bridge between two Cu^+ ions.

The α-$KAgTeS_3$ compound has a centrosymmetrical layered structure. The most substantial difference in the structures of the α and β phases consists in the difference in the arrangement of the pyramidal TeS_3^{2-} ions. In the structure of α-$KAgTeS_3$, the tellurium atoms are located on the surface of the layers so that their lone electron pairs are directed away from the layer. Neither silver ions nor alkali metals interact with these lone pairs. On the contrary, the K^+ ions are surrounded by seven sulfur atoms.

The crystals of $CsCuTeS_3$ belong to the cubic system. In the crystal structure, the $CuTeS_3^-$ ions are linked to each other to form a three-dimensional non-centrosymmetrical chain. The Cu^+ ions have a planar-trigonal coordination. Each CuS_3 triangle is linked to three adjacent TeS_3^{2-} pyramids *via* shared vertices and *vice versa*. The crystallographically equivalent sulfur atoms are linked through the copper and tellurium atoms at an angle of $\sim 90^\circ$.

All compounds of the trithiotellurides series satisfy Zintl's criterion, which accounts for their dielectric properties. The optical measurements revealed the presence of the forbidden band in the region from 1.95 eV ($RbCuTeS_3$) to 2.2 eV (α-$KAgTeS_3$).

Kanatzidis [140] summarised a rare experience in the field of inorganic chemistry of tellurium and noted that this division of synthetic and structural chemistry of chalcogenides is characterised by the fact that both the compositions and structures of tellurides are unpredictable. However, even from the available data it is clear that ternary copper and silver tellurides are very promising material because they show diverse physical properties (from dielectric to semiconducting), possess interesting magnetic properties and exhibit transitions to states with CDWs. These transitions, which attracted the attention of chemists only early in the 1970s, comprise a new exciting field of solid-state chemistry because they are closely associated with the problem of the variable valence and charge ordering in crystals. The detailed consideration of this problem is beyond the scope of this review. Let us only mention the small but rather informative review devoted to this problem. [143]

V. Conclusion

As is evident from the present review, the chemistry of ternary copper chalcogenides, which has progressed in the last decade, shows promise from the viewpoint of the development of new materials with a broad spectrum of electrophysical properties, including new high-temperature superconductors. In essence, only ternary copper and silver chalcogenides containing ions of alkali or alkaline-earth metals as well as thallium have been systematically studied. Data on physicochemical properties of ternary Ln–Cu–X chalcogenides (Ln is a rare-earth element), which are analogues of high-temperature superconductors, are scarce. This field of research is in its infancy. In 1994, the first mixed copper chalcogenides containing cerium, *viz*., $KCuCe_2S_6$ and KCu_2CeS_4, were synthesised.[144, 145] Both sulfides were prepared from $K_2S-Cu-Ce-S$ melts and have layered structures. Their compositions do not satisfy Zintl's criterion (it is highly improbable that cerium in sulfides has the degree of oxidation of +4). However, both salts exhibit dielectric properties; the width of the forbidden band in $KCuCe_2S_6$ is 1.8 eV. In $K_2Cu_2CeS_4$, the gap was not found in the range of 250–2500 nm. The conductivity of this salt at 293 K ($\sigma_{RT} \sim 10^{-3}\ \Omega^{-1}\ cm^{-1}$) is five orders of magnitude larger than that of the $KCuCe_2S_6$ salt. However, the temperature dependence of the electrical resistance is typical of semiconductors. The thermoelectromotive force of crystals of the $K_2Cu_2CeS_4$ salt has a plus sign and the thermoelectromotive force decreases as the temperature decreases, which may be indicative of the metallic state. However, the thermoelectromotive force is much larger than the expected value for a metal.

Based on these facts as well as on the results of magnetic measurements, the authors [144] proposed the following formulas for mixed sulfides: $K^+Cu^+(Ce^{3+})_2(S^{2-})_2(S_2^{2-})_2$ for $KCuCe_2S_6$ and $K_2^+(Cu^+)_2Ce^{3+}(S^{2-})_3(S^-)$ for $K_2Cu_2CeS_4$. The magnetic susceptibility of the $KCuCe_2S_6$ salt obeys the Curie–Weiss law (the Weiss constant $\theta = -67$ K), $\mu_{eff} = 3.1\mu_B$, which is close to the purely spin value of $2.83\mu_B$ for two unpaired electrons (one electron from each Ce^{3+} ions). A more complex situation arises with sulfide $K_2Cu_2CeS_4$. For this compound, either the $K_2^+Cu^+Cu^{2+}Ce^{3+}S_4^{2-}$ structure with the mixed-valence state for copper or the above-mentioned structure containing 'holes' in the *p* band formed by the 3*p* orbitals of the sulfur atoms has to be postulated. According to the approach accepted in our works, the mixed-valence states both of sulfur and copper atoms should be considered, as in the case of the above-considered chalcogenides, taking into account substantially covalent interactions between copper and sulfur atoms.

However, the absence of metallic properties in sulfide $K_2Cu_2CeS_4$ seems to be strange. Sutorik *et al.*[144] attributed this situation to the fact that the peculiarities of the crystal structure of this compound lead to the formation of a very narrow band, which, in turn, results in the formation of low-lability polarons in the presence of highly charged ions, such as Ce^{3+} ions in the case under consideration.

In the case of sulfides $KCuCe_2S_6$ and $K_2Cu_2CeS_4$, the combination of rare-earth elements and the alkali metal does not lead to an increase in the degree of oxidation of copper, unlike high-temperature superconductors. The reason is that the electronegativity decreases in going from oxygen to sulfur. Besides, as is evident from the present review, no copper sulfides (neither binary nor mixed) containing only Cu^{2+} ions are known.

Two years later,[146] sulfide $KCuEu_2S_6$ was synthesised. This salt contains double layers formed by the EuS_8 polyhedra (bicapped trigonal prisms) and the CuS_4 polyhedra (tetrahedra) linked to each other. The authors did not perform electrophysical measurements. However, judging from the dark-brown colour of the crystals, it is believed that this sulfide is a narrow-band semiconductor.

The manifestation of the effect of the chalcogen content on the physical properties of mixed copper oxides and sulfides is also different. It is known [10] that in oxides, such as, for example, La_2CuO_{4-x} or $YBa_2Cu_3O_{6.5+x}$, the degree of oxidation of copper increases as the oxygen content increases. Sulfide analogues of oxides La_2CuO_{4-x} and $Y_2Cu_2O_5$ were synthesised [147] with the aim of elucidating the effect of the anionic subsystem on the electrophysical properties of chalcogenides based on copper. Sulfides La_2CuS_{4+x} and $Y_2Cu_2S_{5+x}$ were prepared by fusing a mixture of Ln_2S_3, CuS and S at 800–900 °C. Their individuality was confirmed by X-ray diffraction studies. The X-ray photoelectron spectra have doublets in the region of the *E*S(2*p*) values. One of these doublets at 161.8 eV corresponds to the S^{2-} ions [82] and the second doublet at 162.8 eV can be assigned to the S_2^{2-} ions. In the *E*Cu($2p_{3/2}$) region, the lines at 932.6 eV correspond to the Cu^+ ions. According to the data of X-ray photoelectron spectroscopy, a decrease in the sulfur content in samples upon annealing

in vacuo occurs as follows: lines at 934.5 eV, which correspond to the Cu^{2+} ions, appear and intensities of the lines corresponding to the disulfide ions decrease.

Samples of La_2CuS_{4+x} saturated with sulfur have the composition La_2CuS_5. Based on the results of X-ray photoelectron spectroscopy, their structures can be represented by the formula $La_2^{3+}Cu^{+}(S_2^{2-})_{1.5}(S^{2-})_2$. Sulfide La_2CuS_5 exhibits dielectric properties. When sulfur is removed until the sample acquires the composition La_2CuS_4, the degree of oxidation of copper increases and the content of disulfide ions decreases. The appearance of the mixed-valence state of copper leads to the nonmetal–metal transition. The temperature dependence of the electrical resistance of samples of La_2CuS_4 is typical of metals. Below 100 K, the temperature dependence of the resistance is nonlinear.

Sulfide $Y_2Cu_2S_{5+x}$, which is maximum saturated with sulfur, has the composition $Y_2Cu_2S_5$. Its X-ray photoelectron spectrum has lines at 932.8 and 934.5 eV belonging to the Cu^{+} and Cu^{2+} ions.[82] Sulfur is present as the S^{2-} and S_2^{2-} ions [$ES(2p)$ = 161.8 and 162.8 eV, respectively]. The $\rho(T)$ dependence is typical of metals (Fig. 32). When sulfur is removed until the compound acquires the composition $Y_2Cu_2S_4$, this dependence becomes more complex and goes through a weak maximum at $T \sim 240$ K. According to the results of X-ray photoelectron spectroscopy, this sample contains sulfur only as sulfide ions and the $Cu^{+}:Cu^{2+}$ ratio decreases from 3 : 1 in the initial sample to 1 : 1 in the final product.[148]

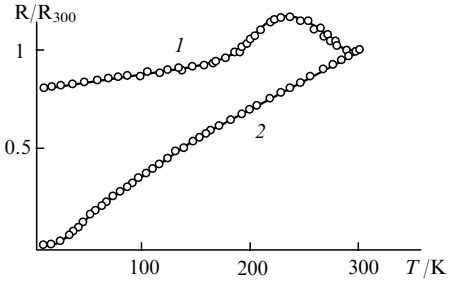


Figure 32. Temperature dependence of the electrical resistance of samples of $Y_2Cu_2S_4$ (*1*) and $Y_2Cu_2S_5$ (*2*).[148]

Hence, in the case of sulfides, the situation is opposite to that observed in oxides. The possible reasons for this fact are the lower electronegativity of sulfur responsible for reducing properties of the sulfide ion,

$$2S^{2-} - 2e \longrightarrow S_2^{2-}$$

as well as the reaction

$$S + S^{2-} \longrightarrow S_2^{2-},$$

in the course of which excess sulfur is bound by sulfide ions rather than oxidises Cu^{+} ions.

Apparently, these processes are hindered when the sulfur content is decreased and, as a consequence, the degree of oxidation of sulfur decreases as its content decreases.

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References

1. J G Bednorz, K A Müller *Z. Phys.* **B64** 187 (1986)
2. C W Chu, L Gao, F Chen, Z J Huang, R L Meng, Y Y Xue *Lett. Nature* **365** 323 (1993)
3. M Lagues, Xiao Ming Xie, H Tebbi, Xiang Zhen Xu, V Mairet, Ch Hatterer, C F Beuran, C Deville-Cavellin *Science* **262** 1850 (1993)
4. R S Burrows, D H McDaniel *Angew. Chem., Int. Ed. Engl.* **33** 897 (1994)
5. P W Anderson *Science* **235** 1196 (1987)
6. M J S Dewar *Angew. Chem, Int. Ed. Engl.* **26** 1273 (1987)
7. W Urland *Angew. Chem., Int. Ed. Engl.* **26** 1275 (1987)
8. S R Ovshinsky *Chem. Phys. Lett.* **195** 455 (1992)
9. A Villesuzanne, M Pouchard *C. R. Hebd. Seances Acad. Sci., Ser. 2* **322** 155 (1996)
10. V V Nemoshkalenko, V N Uvarov, A A Ereshchenko, S K Tolpygo, V A Starodub, M A Obolenskii, A V Zhalko-Titarenko, L M Sheludchenko *Sverkhprovod. Fiz. Khim. Tekhn.* **3** 856 (1990)
11. I Panas, R Gatt *Chem. Phys. Lett.* **270** 178 (1997)
12. A Simon *Angew. Chem.* **109** 1872 (1997)
13. I Panas, R Gatt *Chem. Phys. Lett.* **266** 410 (1997)
14. R Cloots, A Rulmont, P A Godelaine, C Hannau, H W Vanderschueren, M Auslos *Solid State Commun.* **79** 615 (1991)
15. C N R Rao, J Gopalakrishnan *New Directions in Solid State Chemistry* (Cambridge: Cambridge University Press, 1986)
16. B W Roberts *Properties of Selected Superconductive Materials. 1978. Supplement National Bureau of Standards* (Ed. B W Roberts) (Washington, DC: US Government Printing Office, 1978) p. 983
17. A F Wells *Structural Inorganic Chemistry* (Oxford: Clarendon Press, 1986)
18. S Robashkiewicz, M Zimpel, I Onyshriewicz, M A Obolensky *Acta Magnetica* **8** 58 (1991)
19. M G Kollin, F Rouyer, J Loriers *C. R. Hebd. Seances Acad. Sci., Ser. C* **266** 689 (1968)
20. M Julien-Pouzol, M Guittard, M A Mazurier *Acad. Sci., Paris* **271** C1317 (1970)
21. M Julien-Pouzol, M Guittard *Ann. Chim.* **7** 253 (1972)
22. O V Andreev *Zh. Neorg. Khim.* **33** 991 (1988) [a]
23. O V Andreev, N N Parshukov *Zh. Neorg. Khim.* **36** 2106 (1991) [a]
24. W J Zhu, Y Z Huang, C Dong, Z X Zhao *Mater. Res. Bull.* **29** 143 (1994)
25. B A Popovkin *Zh. Neorg. Khim.* **38** 2020 (1993) [a]
26. Yu M Yarmoshenko, V A Trofimova, V E Dolgih, M A Korotin, E Z Kurmaev, J A Aguiar, J M Ferreira, A C Pavao *J. Phys., Condens. Matter* **7** 213 (1995)
27. D N Argiriou, J D Jorgensen, R L Hitterman, Z Hiroi, N Kobayashi, M Takano *Phys. Rev. B, Condens. Matter* **51** 8434 (1995)
28. W A Starodub, M A Obolensky, Kh B Chashka, K V Krikunov, Yu B Poltoratsky, S Robashkiewicz, in *Proceedings of International Conference on High Temperature Superconductivity and Localisation Phenomena (Abstracts of Reports), Moscow, 1991* p. C14
29. M Draganjac, T B Rauchfuss *Angew. Chem., Int. Ed. Engl.* **24** 742 (1985)
30. A Müller, U Schimanski *Inorg. Chim. Acta* **77** L187 (1983)
31. A Müller, F-W Baumann, H Bögge, M Römer, E Krickemeyer, K Schmitz *Angew. Chem.* **96** 607 (1984)
32. A Müller, M Römer, E Krickemeyer, F-W Baumann, K Schmitz *Inorg. Chim. Acta* **89** L7 (1984)
33. A Müller, M Römer, E Krickemeyer, H Bögge *Naturwissenschaften* **71** 43 (1984)
34. A Müller, M Römer, H Bögge, E Krickemeyer, K Schmitz *Inorg. Chim. Acta* **85** L39 (1984)
35. G Henkel, P Betz, B Krebs *J. Chem. Soc., Chem. Commun.* 314 (1984)
36. A Müller, M Römer, H Bögge, E Krickemeyer, D Bergmann *J. Chem. Soc., Chem. Commun.* 348 (1984)
37. P Betz, B Krebs, G Henkel *Angew. Chem., Int. Ed. Engl.* **23** 311 (1984)
38. G Marbach, J Strähle *Angew. Chem., Int. Ed. Engl.* **23** 715 (1984)
39. S-P Huang, M G Kanatzidis *Angew. Chem., Int. Ed. Engl.* **31** 787 (1992)
40. H Krautscheid, D Fenske, G Baum, M Semmelmann *Angew. Chem., Int. Ed. Engl.* **32** 1303 (1993)
41. M G Kanatzidis, S-P Huang *Inorg. Chem.* **28** 4667 (1989)
42. S-P Huang, M G Kanatzidis *Inorg. Chem.* **30** 3572 (1991)
43. K-W Kim, M G Kanatzidis *J. Am. Chem. Soc.* **115** 5871 (1993)
44. A Müller, E Krickemeyer, M Zimmermann, M Römer, H Bögge, M Penk, K Schmitz *Inorg. Chim. Acta* **90** L69 (1984)
45. S-P Huang, M G Kanatzidis *Inorg. Chem.* **30** 1455 (1991)
46. J Cusick, M L Scudder, D G Craig, I G Dance *Polyhedron* **8** 1139 (1989)
47. U Müller, M L Ha-Eierdanz, G Kriuter, K Z Dehnicke *Z. Naturforsch., B Chem. Sci.,* **45** 1128 (1990)
48. G Marbach, J Strähle *Angew. Chem., Int. Ed. Engl.* **23** 246 (1984)
49. R C Haushalter *Angew. Chem., Int. Ed. Engl.* **24** 432 (1985)
50. C J Warren, D M Ho, A B Bocarsly, R C Haushalter *J. Am. Chem. Soc.* **115** 6416 (1993)
51. R C Haushalter *Inorg. Chim. Acta* **102** L37 (1985)

52. M A Ansari, J C Bollinger, J A Ibers *J. Am. Chem. Soc.* **115** 3838 (1993)
53. J M McConnachie, M A Ansari, J C Bollinger, R J Salm, J A Ibers *Inorg. Chem.* **32** 3201 (1993)
54. M A Ansari, J M McConnachie, J A Ibers *Acc. Chem. Res.* **26** 574 (1993)
55. R D Harcourt *J. Inorg. Nucl. Chem.* **39** 237 (1977)
56. M A Ansari, J C Bollinger, J A Ibers *Inorg. Chem.* **32** 1746 (1993)
57. K A Hofmann, F Hochtlen *Ber. Dtsch. Chem. Ges.* **36** 3090 (1903)
58. M G Kanatzidis, Y Park *J. Am. Chem. Soc.* **111** 3767 (1989)
59. Ch Z Burschka *Z. Naturforsch., B Chem. Sci.* **35** 1511 (1980)
60. G Gattow, T Dingeldein *Z. Anorg. Allg. Chem.* **596** 73 (1991)
61. G Kiel, G Gattow, T Dingeldein *Z. Anorg. Allg. Chem.* **596** 111 (1991)
62. R M H Banda, D C Craig, J G Dance, M L Scudder *Polyhedron* **8** 2379 (1989)
63. M G Kanatzidis, S-P Huang *Angew. Chem., Int. Ed. Engl.* **28** 1556 (1989)
64. T J McCarthy, X Zhang, M G Kanatzidis *Inorg. Chem.* **32** 2944 (1993)
65. M G Kanatzidis, S-P Huang *J. Am. Chem. Soc.* **111** 760 (1989)
66. P T Wood, W T Pennington, J W Kolis *J. Am. Chem. Soc.* **114** 9233 (1992)
67. L C Roof, J W Kolis *Chem. Rev.* **93** 1037 (1993)
68. P T Wood, W T Pennington, J W Kolis *J. Chem. Soc., Chem. Commun.* 235 (1993)
69. Y Park, M G Kanatzidis *Angew. Chem., Int. Ed. Engl.,* **29** 914 (1990)
70. K O Klepp, W Bronger *J. Less-Common Met.* **127** 65 (1987)
71. P Pekka *Kem.-Kemi* **8** 498 (1981)
72. D E Bacelo, S D Huang, Y Ishikawa *Chem. Phys. Lett.* **277** 215 (1997)
73. S Loeken, C Felser, W Tremel *J. Chem. Soc., Chem. Commun.* 1603 (1998)
74. Pyykko Pekka, J Li, N Runeberg *Chem. Phys. Lett.* **218** 133 (1994)
75. M G Kanatzidis *Chem. Matter.* **2** 353 (1990)
76. C C Raymond, P K Dorhout *Inorg. Chem.* **35** 5634 (1996)
77. J C Folmer, F Jellinek *J. Less-Common Met.* **76** 153 (1980)
78. H J Gotsis, A C Barnes, P Strange *J. Phys., Condens. Matter* **4** 10 461 (1992)
79. W Liang, M H Whangbo *Solid State Commun.* **85** 405 (1993)
80. G V Vajenine, R Hoffmann *Inorg. Chem.* **35** 451 (1996)
81. Georg Brauer (Ed.) *Handbuch der Preparativen Anorganischen Chemie* Bd. 2 (Stuttdart: Ferdinand Enke Verlag, 1978)
82. V I Nefedov *Rentgenoelektronnaya Spektroskopiya Khimicheskikh Soedinenii* (X-Ray Electron Spectroscopy of Chemical Compounds) (Moscow: Khimiya, 1984)
83. A Ouammou, M Mouallem-Bahout, O Pena, J F Halet, J Y Saillard, C Carel *J. Solid State Chem.* **117** 73 (1995)
84. K Klepp, H Boller *Monatsh. Chem.* **109** 1049 (1978)
85. R Berger *J. Less-Common Met.* **147** 141 (1989)
86. K Klepp, H Boller, H Völlenkle *Monatsh. Chem.* **111** 727 (1980)
87. D B Brown, J A Zubieta, P A Vella, J T Wrobleski, T Watt, W E Hatfield, P Day *Inorg. Chem.* **19** 1945 (1980)
88. C Burschka *Z. Anorg. Allg. Chem.* **463** 65 (1980)
89. R Berger, L Eriksson *J. Less-Common Met.* **161** 165 (1990)
90. G Brun, B Gardes, J C Tedenac, A Raymond, M Maurin *Mater. Res. Bull.* **14** 743 (1979)
91. R Berger, C F Van Bruggen *J. Less-Common Met.* **99** 113 (1984)
92. L Karlsson, M P Keane, R Berger *J. Less-Common Met.* **166** 353 (1990)
93. J E Iglesias, K E Pachali, H Steinfink *J. Solid State Chem.,* **9** 6 (1974)
94. M Saeki, M Onoda, H Kozaki *Mater. Res. Bull.* **23** 603 (1988)
95. M Onoda, M Saeki *Mater. Res. Bull.* **24** 1337 (1989)
96. M V Savel'eva, I N Trushnikova, A A Kamarzin, V I Alekseev, I A Baidina, S V Borisov, S A Gromilov, A G Blinov *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* (3) 157 (1989)
97. G Savelsberg, H Schaefer *Z. Naturforsch., B Chem. Sci.* **33** 370 (1978)
98. G Savelsberg, H Schaefer *Z. Naturforsch., B Chem. Sci.* **33** 711 (1978)
99. W Rüdorff, H G Schwarz, M Walter *Z. Anorg. Allg. Chem.* **269** 141 (1952)
100. B P Ghosh, M Chaudhury, K Nag *J. Solid State Chem.* **47** 307 (1983)
101. N S Hartig, P K Dorhout, S M Miller *J. Solid State Chem.* **113** 88 (1994)
102. W Bronger *Angew. Chem., Int. Ed. Engl.* **20** 52 (1981)
103. F Viola, R Schollhorn *J. Chem. Soc., Chem. Commun.* 907 (1992)
104. G Savelsberg, H Schaefer *Mater. Res. Bull.* **16** 1291 (1981)
105. H Effenberger, F Pertlik *Monatsh. Chem.* **116** 921 (1985)
106. J E Iglesias, K E Pachali, H Steinfink *Mater. Res. Bull.* **7** 1247 (1972)
107. W Bronger, B Lenders, J Huster *Z. Anorg. Allg. Chem.* **623** 1357 (1997)
108. P T Wood, W T Pennington, J W Kolis *Inorg. Chem.* **33** 1556 (1994)
109. W Bronger, J Eyck, H Schils *J. Less-Common Met.* **60** 5 (1978)
110. W Bronger, C Burschka *Z. Anorg. Allg. Chem.* **425** 109 (1976)
111. C Burschka, W Bronger *Z. Anorg. Allg. Chem.* **430** 61 (1977)
112. C Burschka, W Bronger *Z. Naturforsch., B Chem. Sci.* **32** 11 (1077)
113. K Klepp, K Yvon *Acta Crystallogr., Sect. B* **36** 2389 (1980)
114. R Berger *J. Solid State Chem.* **70** 65 (1987)
115. R Berger *Chem. Scr.* **28** 41 (1978)
116. R Berger, R V Bucur *Mater. Res. Bull.* **27** 439 (1992)
117. R Berger, R Dronkowski, L Noren *J. Solid State Chem.* **112** 120 (1994)
118. I Jacyna-Onyszkiewicz, M Sidowski, W Starodub, A Ratuszna, S Robaszkiewicz, in *Proceedings of the European Conference on Physics of Magnetism, Wroclaw, 1996* p. 105
119. C Burschka *Z. Naturforsch., B Chem. Sci.* **34** 396 (1979)
120. Z Perlinski, D B Brown, T Watt, W E Hatfield, P Day *Inorg. Chem.* **21**1752 (1982)
121. V A Starodub, I V Krivoshei *Usp. Khim.* **51** 764 (1982) [*Russ. Chem. Rev.* **51** 439 (1982)]
122. M-H Whangbo, E Canadell *Inorg. Chem.* **29** 1395 (1990)
123. X Zhang, M G Kanatzidis *J. Am. Chem. Soc.* **118** 693 (1996)
124. I Jacyna-Onyszkiewicz, M Sidowski, W Starodub, A Ratushna, S Robaszkiewicz, in *Proceedings of the European Conference on Physics of Magnetism, Wroclaw, 1996* p. 79
125. Y Furukawa, S Wada, K Miyatani, T Tanaka, M Fukugauchi, M Ishikawa *Phys. Rev. B, Condens. Matter* **51** 6159 (1995)
126. R Brusetti, O Laborde, A Sulpice, R Calemczuk, M Potel, P Cougeon *Phys. Rev. B, Condens. Matter* **52** 4481 (1995)
127. T Hagino, Y Seki, N Wada, S Tsuji, T Shirane, Ken-ichi Kumagai, S Nagata *Phys. Rev. B, Condens. Matter* **51** 12673 (1995)
128. R Schneider *J. Prakt. Chem.* **108** 16 (1865)
129. C Burschka *Z. Naturforsch., B Chem. Sci.* **34** 675 (1979)
130. L W Ter Haar, F J DiSalvo, H E Bair, R M Fleming, J V Waszczak *Phys. Rev. B, Condens. Matter* **35** 1932 (1987)
131. H Schils, W Bronger *Z. Anorg. Allg. Chem.* **456** 187 (1979)
132. R M Fleming, L W Ter Haar, F J DiSalvo *Phys. Rev. B, Condens. Matter* **35** 5388 (1987)
133. K O Klepp *J. Less-Common Met.* **128** 79 (1987)
134. B Gardes, S Peytavin, M Maurin *C. R. Hebd. Seances Acad. Sci., Ser. C* **283** 529 (1976)
135. Y Park, D C Degroot, J Schindler, C R Kannewurf, M G Kanatzidis *Angew. Chem., Int. Ed. Engl.* **30** 1325 (1991)
136. S Seong, T A Albright, X Zhang, M Kanatzidis *J. Am. Chem. Soc.* **116** 7287 (1994)
137. X Zhang, Y Park, T Hogan, J L Schindler, C R Kannewurf, S Seong, T Albright, M G Kanatzidis *J. Am. Chem. Soc.* **117** 10 300 (1995)
138. X Zhang, J L Schindler, T Hogan, J Albritton-Thomas, C R Kannewurf, M G Kanatzidis *Angew. Chem., Int. Ed. Engl.* **34** 68 (1995)
139. X Zhang, J Li, B Foran, S Lee, Hong-You Guo, T Hogan, C R Kannewurf, M G Kanatzidis *J. Am. Chem. Soc.* **117** 10 513 (1995)
140. M G Kanatzidis *Angew. Chem., Int. Ed. Engl.* **34** 2109 (1995)
141. R Kniep, H-J Beister *Angew. Chem., Int. Ed. Engl.* **24** 393 (1985)
142. X Zhang, M G Kanatzidis *J. Am. Chem. Soc.* **116** 1890 (1994)
143. S P Ionov *Zh. Fiz. Khim.* **56** 2385 (1982) [b]
144. A C Sutorik, J Albritton-Thomas, C R Kannewurf, M G Kanatzidis *J. Am. Chem. Soc.* **116** 7706 (1994)
145. M A Pell, J A Ibers *Chem. Ber.* **130** 1 (1997)
146. W Bensch, P Dmrichen *Chem. Ber.* **129** 1489 (1996)
147. I Jacyna-Onyszkiewicz, M Zimpel, V Starodub, S Robaszkiewicz *Mol. Phys. Rep.* **12** 115 (1995)
148. V A Starodub, Doctoral Thesis in Chemical Sciences, Khar'kov State University, Khar'kov, 1994

[a] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[b] — *Russ. J. Phys. Chem. (Engl. Transl.)*