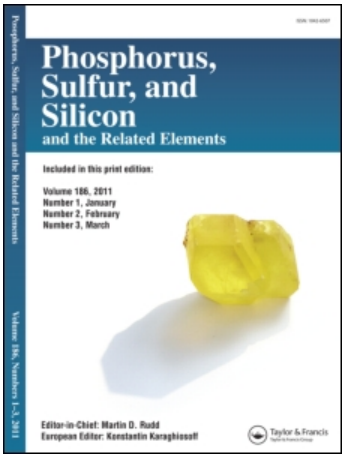

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CHALCOGENE-RICH CHALCOGENIDES: FROM THE FIRST IDEAS TO A STILL GROWING FIELD OF RESEARCH

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A brief survey of a method of classification of chalcogene-rich chalcogenides is given. The anionic patterns of the compounds are either considered as isostructural derivatives of noble gas fluoride and interhalogene basic fragments or are due to high symmetric square sheets and primitive cubic networks. With the increasing number of precise investigations on new compounds the underlying principle of the classification becomes more evident. Small deviations, nearly always observed in the structures, can often be explained by electronic requirements.

Keywords: polychalcogenides; crystal structures

INTRODUCTION

A couple of years ago the expression tellurium-rich tellurides has been introduced in order to distinguish a new class of tellurium compounds MTe_n from the so called polychalcogenides MX_n ($n > 2$; X = S, Se, Te)[1]. The polychalcogenides are characterised by the well known oligomeric anionic chains X_n^{2-}, whereas the tellurium-rich tellurides

very often exhibit one-, two-, or three-dimensional infinite anions. The bond distances and bond angles differ markedly from those observed in the classical polychalcogenides. Selenium usually reacts like sulfur to give polyselenides but in some cases a behaviour similar to tellurium in the tellurium-rich tellurides is found. Hence, we will discuss these selenides and tellurides briefly and denote them as chalcogene-rich chalcogenides. For more detailed information and discussions the reader is referred to the references cited in this paper.

In table I the most representative examples of these compounds are listed. Main group metal compounds are shown in the left and transition metal compounds in the right column, respectively (references are given in the text). Until the mid-seventies nearly no main group metal tellurides were known, whereas the number of transition metal chalcogenides was slightly larger. The interests of chemists, physicists, and crystallographers were focussed on the latter compounds immediately after their discovery due to some special physical properties. The rare earth tellurides $LnTe_n$ synthesised in the mid-sixties show metallic behaviour depending on the amount of tellurium layers in their structures[1,2].

TABLE I

main group metals		transition metals
	1961	
	1962	
	1963	
	1964	$CuTe$, MTe_4 (M = Nb, Ta)
	1965	$LnTe_n$ (n = 2, 2.5, 3)
	1966	
	1967	
	1968	
$MgTe_2$	1969	
	1970	UTe_2
	1971	
	1972	
	1973	MTe_5 (M = Zr, Hf)
$TlTe$	1974	
	1975	MX_3 (M = Zr, Nb, Ta; X = Se, Te)
In_2Te_5	1976	
$LiTe_3$, Ga_2Te_5	1977	
	1978	
	1979	
	1980	
	1981	
Cs_2Te_5, $BaBiTe_3$	1982	$CrTe_3$, $AgTe_3$
Rb_2Te_5, K_2SnTe_5	1983	Re_2Te_5
	1984	UTe_5
$CsTe_4$, Rb_2SnTe_5, $NaTe$, $(Te_2)_2I_2$	1985	
$NaTe_3$, Ba_2SnTe_5	1986	
	1987	
	1988	
Cs_4Se_{16}, $[PPh_4]_2Se_{11}$	1989	
Tl_2GeTe_5, $[PNP]_2Se_{10}$	1990	
Tl_2SnTe_5	1991	$LaSe_{2-x}$
	1992	
$[K(15C5)]_2Te_8$	1993	$Rb_{0.33}DySe_{2.67}$, $DySe_{2-x}$
$LiSe_3$, $RbTe_6$	1994	
Cs_3Te_{22}, $K_{0.33}Ba_{0.67}AgTe_2$	1995	
Cs_2Te_{13}, Cs_4Te_{28}, $[Net_4]_2Te_{12}$,	1996	U_2Te_5, UTe_3, $Cs_{0.5}ThTe_3$
	1997	$U_{1-x}Te_3$, $[Cr(en)_3]Te_6$, $Tl_{0.56}UTe_3$

The tetratellurides of niobium and tantalum MTe_4, the trichalcogenides MX_3 of the groups 4 and 5 and the pentatellurides of zirconium and hafnium MTe_5 are materials with quasi one-dimensional structures and some further interesting physical properties[2b,3]. Nevertheless, almost no attention had been paid to tellurium

interactions according to Te–Te distances larger than about 2.8 Å although these interactions had been noticed in a few cases.

The situation in main group tellurides was somewhat different. The only Te–Te distances found in TlTe[4] for instance, are in the range of 3.05 Å and therefore they could not be ignored. To discuss the structure of $LiTe_3$[5] the authors refer to a hypothetical metal-like cubic primitive tellurium structure as a precursor. Consequently, they describe the structure as a "mixture" of polytelluride-like parts with bent Te_n^{2-} units (Te–Te: 2.86–3.02 Å) and parts of a hypothetical tellurium modification of cubic primitive structure (Te···Te: 3.14 – 3.32 Å). Last, but not least, the Te–Te distances of 3.03 Å found in Ga_2Te_5[6] had been recognised by the authors.

Possibly due to the small number of examples until the late seventies there was no general conception for treating the tellurides of this type. However, the time had come to try to understand the differences of the structures of the classical polychalcogenides and the chalcogene-rich chalcogenides.

A NEW LOOK AT THE STRUCTURES

A small paper published by Burdett in 1982[7] entitled "New Ways to Look at Solids" was extremely helpful to understand the structures of $AgTe_3$[8] and Cs_2Te_5[9] also published in 1982, as well as those of Re_2Te_5[10], K_2SnTe_5[11], and Rb_2Te_5[12], all published in 1983. In order to discuss the structures of the simple binary alkali metal

pentatellurides M_2Te_5 (M = Rb, Cs) the Te–Te distances of 3.05 Å must be taken into consideration. Moreover their importance for understanding the structures became evident (figure 1). If these distances would be ignored the compounds should be composed of Te_2^{2-}-dumbbells and Te^{2+} cationic species according to M_2Te_5 = 2 M^+ + 2 Te_2^{2-} + Te^{2+}. Obviously this description is not satisfying. But if one considers the Te–Te distances mentioned above to be bonding interactions one-dimensional infinite chains appear: M_2Te_5 = 2 M^+ + $^1_\infty[Te_5^{2-}]$. As a consequence, a XeF_4-like fragment is the only unit needed to build the chains. This basic fragment is shown in figure 1 (inlet), too.

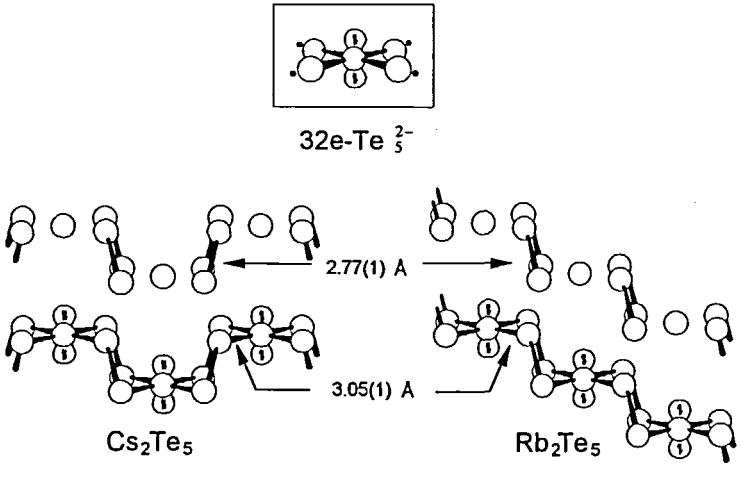

FIGURE 1 Anionic strings of the structures of M_2Te_5 (M = Rb, Cs). The infinite polyanions appear if the Te–Te distances of 3.05 Å are considered as bonding ones.

Doing this some questions arise. Square planar XeF_4 has 36 valence electrons whereas 32e-AB_4 entities are usually found to be tetrahedral ($SnTe_4^{4-}$, AsS_4^{3-}, SO_4^{2-}, ...)[1]. Surprisingly, 32e-$TeTe_4^{2-}$ is square planar again. We would propose that this unexpected shape is stabilised by interconnecting the fragments via their terminal tellurium atoms in order to compensate its lack of electrons. And that is what we observe in the structures. The conclusion could be proofed if a compound composed of quasi-molecular 36e-$TeTe_4^{6-}$ entities existed. This unit, isoelectronic to XeF_4, should be found even in the solid state if the new ideas are meaningful. Fortunately, such a compound was known since 1977.

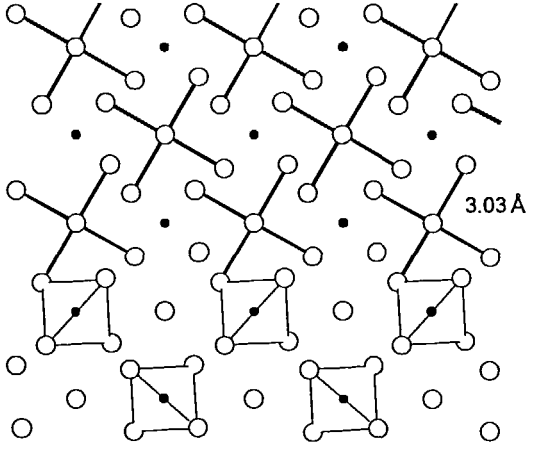

FIGURE 2 Section of the structure of Ga_2Te_5 (black circles: Ga; open circles: Te); top: isolated Te_5^{6-} groups; bottom: some of the (interconnected) $GaTe_{4/2}$ tetrahedra.

The structure of Ga_2Te_5[6] can be understood according to Ga_2Te_5 = 2 Ga^{3+} + Te_5^{6-} (figure 2). The upper part of figure 2 shows the isolated 36e-$TeTe_4^{6-}$ anions (Te–Te: 3.03 Å) as the result of the reinterpretation using the new conception. In the lower part a section of the structure is depicted to illustrate the more conventional way of discussion preferred by the authors. The structure then consists of interconnected $GaTe_{4/2}$ tetrahedra.

Further Structures based on square planar $TeTe_4^{n-}$ units

Additional examples which can be derived from XeF_4, besides M_2Te_5 (M = Rb, Cs) and Ga_2Te_5, are depicted in figure 3. Quasi-molecular isolated 36e-Te_5^{6-} anions as in Ga_2Te_5 are also found in Al_2Te_5[13] and M_2SnTe_5 (M = K, Rb, Tl)[11,14].

Furthermore, a 32e-fragment XX_4^{2-} (X = Se, Te) can not only be stabilised by interconnection as demonstrated for Cs_2Te_5 and Rb_2Te_5, but also by addition of two single tellurium atoms (Re_2Te_5)[10] or two X_3 groups to give anions like Se_{11}^{2-}, $TeSe_{10}^{2-}$, TeS_{10}^{2-} [15] as shown in the right of figure 3. Small finite anions result in these cases. Another very interesting example is $[K(15C5)_2]_2Te_8$[16]. The inner Te_5 core of this compound is completed by a single tellurium atom on one side and a Te_2 bridge on the opposite side. Somewhat unexpected, the Te_7^{2-} anion of Re_2Te_5 is nearly flat although one would expect to find the outermost atoms out of plane as can be seen in the case of the Se_3 groups of $(PPh_4)_2Se_{11}$, for instance[15a]. Another nice example is

Cs_4Se_{16}, where the central Se_5 unit is closed by a Se_3 group on one side only[17].

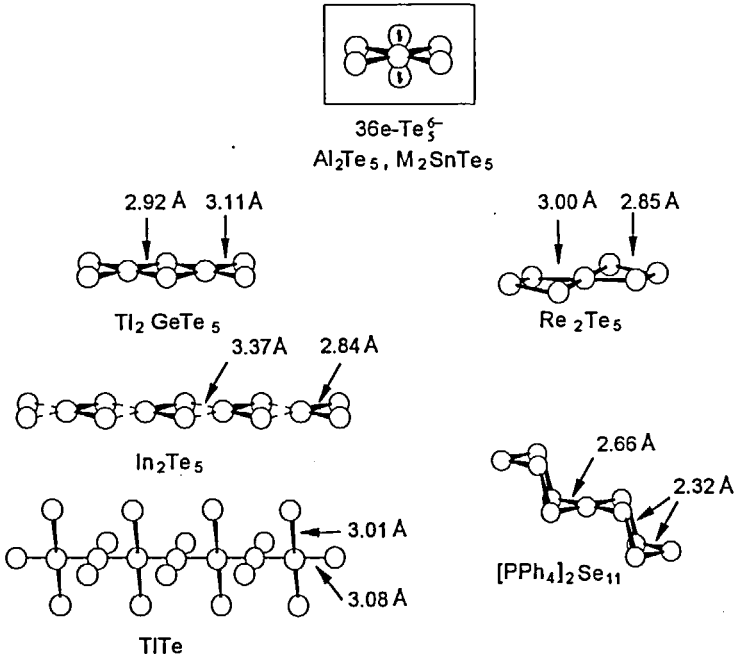

FIGURE 3 Representation of finite (right) and infinite (left) anions, all deducible from a Te_5^{n-} square planar fragment.

A third kind of creating anionic units is shown in the left of figure 3. Now, the basic fragments share some of their terminal atoms to give finite or infinite entities again. Tl_2GeTe_5[18] is characterised by a finite Te_8^{8-} anion according to 2 Tl_2GeTe_5 = 4 Tl^+ + 2 Ge^{4+} + Te_8^{8-} + Te^{2-}. This anion is built of two $[Te_2\,TeTe_{2/2}]^{4-}$ subunits. The shortening of the bond distances of the

central square with respect to the terminal ones should be noticed. Possibly due to this experimental result the authors mention a "square ring of tellurium" but do not discuss this interesting new anion in terms of tellurium-rich tellurides.

Two examples which represent one-dimensional infinite chains are In_2Te_5[13] and TlTe[4]. The Te–Te distances of the infinite chain of In_2Te_5 alternate (2.84 Å and 3.37 Å) as shown in figure 3. Therefore the structure has been described originally as consisting of bent Te_3^{2-} anions (and additional Te^{2-} anions: $In_2Te_5 = 2\ In^{3+} + Te_3^{2-} + 2\ Te^{2-}$; for a discussion of the structure of In_2Te_5 somewhat different from that given here the reader is referred to reference [13]. The authors compare the $InTe_{3/3}Te$ tetrahedra of In_2Te_5 with the $GaTe_{4/2}$ tetrahedra of the original description of the structure of Ga_2Te_5[6]. Nevertheless, figure 3 clearly shows the relationship of the chain depicted to the chalcogene-rich chalcogenides.).

The anionic part of the structure of TlTe consists of two different infinite units. A linear string of equidistant tellurium atoms (Te–Te: 3.08 Å; not depicted in figure 3) and the chain sketched on the bottom left of figure 3. The relationship to the square-planar basic fragment is again clearly to be seen. Some attempts have been made in the past to solve the structure of TlTe, but in our opinion it is not yet known in all its details. The anisotropic displacement parameters of at least one tellurium atom are questionable[4]. Similar anionic fragments as in TlTe are also found in the unique tellurium net of $Rb_{4+x}Sn_4Te_{17}$[17].

Obviously the 36e-XeF_4 molecule is a suitable representative for some examples of this class of compounds. Therefore, the question

arises if other noble gas fluorides such as XeF_2 or even interhalogene compounds XY_n (X = Cl, Br, I; Y = F; n = 1, 3, 5, 7) could also be considered as representatives for further chalcogene-rich chalcogenides. X_2^{2-} dumbbells of chalcogene atoms are isoelectronic with halogenes X_2 or interhalogene compounds XY. These anionic dimers are well known from numerous dichalcogenides of main group and transition metals and will not be discussed in this paper. For further information the reader is referred to reference [19], for instance.

Structures based on linear $TeTe_2^{n-}$ units

The shape of a triatomic AB_2 unit depends strongly on its electron quantity[20]. 20e-X_3^{2-} are bent, found for instance in alkali metal trichalcogenides M_2Te_3 and the alkaline earth trichalcogenides MTe_3[1]. On the other hand, 22e-X_3^{4-} anions, isoelectronic with XeF_2 or I_3^-, are expected to be linear. The result of a calculation[20a] is drawn in the upper left of figure 4. The Walsh diagram shows the stabilisation of a 22e-Te_3^{4-} fragment by increasing the bond angle successively from 90° to 180°. This strong stabilisation is due to the decreasing of the antibonding character of the $5a_1$ band which becomes the HOMO at 180°.

Up to now no striking example with isolated Te_3^{4-} anions is known. But structure and physical properties of $Ca_{0.67}K_4Te_3$[21] can only be understood if a one-dimensional row of triatomic units $\cdots Te_3^{4-} \cdots Te_3^{4-} \cdots Te_3^{4-} \cdots$ is considered as the anionic part instead of an one-dimensional chain of equidistant atoms $\cdots Te^{1.33-} \cdots Te^{1.33-} \cdots Te^{1.33-} \cdots$.

This latter chain has been found in the substructure (space group I4/mcm; $Ca_{0.6}K_4Te_3 = 0.67\ Ca^{2+} + 4\ K^+ + 2\ Te^{2-} + {}^1_\infty[Te^{1.33-}]$). The Te–Te distance of the chain atoms is 3.14(1) Å. Due to the negative charge of -1.33 of each chain atom, the compound could be a metal. But conductivity measurements show this compound to be semiconducting (E_g = 1.0(2) eV). Additional precise X-ray investigations indeed yield a superstructure consistent with the description $3\ Ca_{0.67}K_4Te_3 = 3\ Ca^{2+} + 12\ K^+ + 6\ Te^{2-} + Te_3^{4-}$ (figure 4, upper right). Taking the U_{33} value of the tellurium atoms of the chain ${}^1_\infty[Te^{1.33-}]$, its mean square root of 0.23 Å can be calculated. In dislocating two thirds of the chain atoms by only a third of this value (i. e. 0.08 Å), Te_3^{4-} groups with intramolecular distances of 3.06 Å result, whereas the intermolecular distances increase to 3.30 Å at the same time (figure 4). The superstructure observed can tentatively be assigned to be of site occupancy wave type (SOW)[22].

Additionally, the compounds CuTe[23], UTe_n (n = 2, 2.5, 5)[24] as well as the tellurides of the $ZrSe_3$ type[3,25] show anionic chains with Te–Te distances of about 3.1 Å. Recently two interesting structures were published, $Cs_{0.5}ThTe_3$[26a] and $Tl_{0.56}UTe_3$[26b], both closely related to the $ZrSe_3$ type, too. It should be stated here, that the structures of these compounds are at least isopointal to the selenide $Rb_{0.33}DySe_{3-x}$ (x = 0.33)[22a]. Considering uranium and thorium as M^{4+} cations and dysprosium as Dy^{3+}, the tellurium atoms of the extended polyanions in A_nMTe_3 carrier an excess charge of –1.25, whereas the respective selenium atoms in $Rb_{0.33}DySe_{3-x}$ are $Se^{0.8-}$ only. This is mirrored in the anionic parts of the structures: the actinide tellurides contain linear

chains $\cdots Te^{1.25-}\cdots Te^{1.25-}\cdots Te^{1.25-}\cdots$, whereas the selenide is composed of (defect) square sheets $^{2}_{\infty}[Se_{0.89}\square_{0.11}]$.

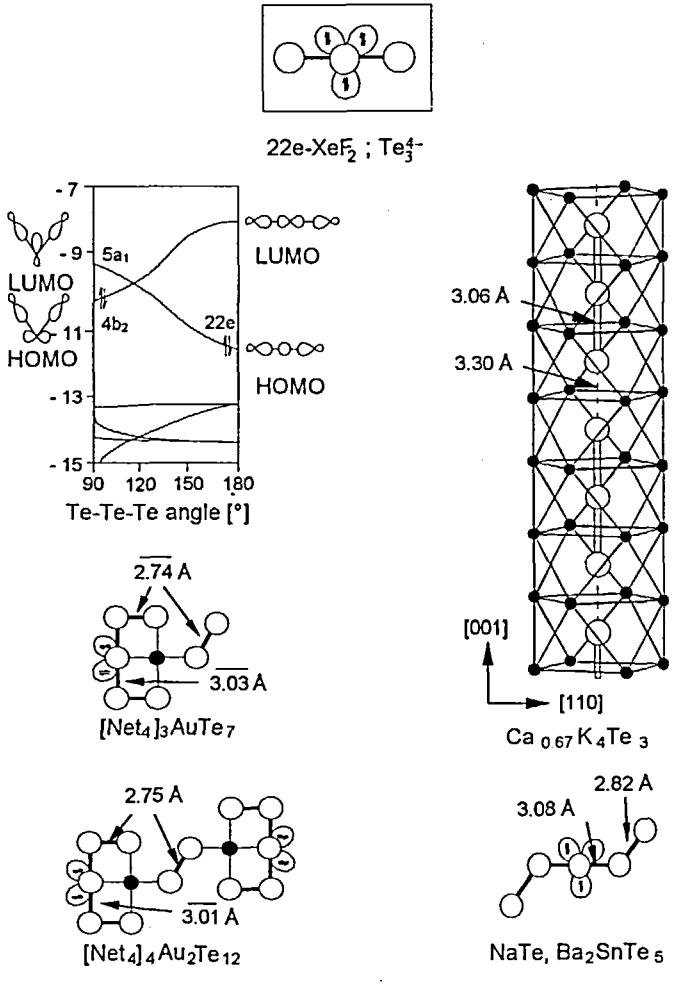

FIGURE 4 Anions based on Te_3^{n-} linear fragments. The calculated shape of a 22e- Te_3^{4-} unit is is shown in the Walsh diagram.

Usually the Te–Te distances of the chains of all these structures alternate slightly. Hence, the anionic parts of these compounds could at least formally be understood as derivatives of a XeF_2 basic fragment. This kind of dependence of the structures on the number of electrons of the chalcogene atoms in the polyanions, as discussed above, has been noticed in reference [1] for the first time.

Going back to the much simpler small units, the 34e-Te_5^{4-} anions found in NaTe (6 NaTe = 6 Na^+ + Te_5^{4-} + Te^{2-})[27] and Ba_2SnTe_5 (3 Ba_2SnTe_5 = 6 Ba^{2+} + $[Sn_3Te_{10}]^{8-}$ + Te_5^{4-})[28] are very instructive examples of an incomplete linear Te_3^{2-} fragment which compensates its lack of electrons by adding two single atoms. Of course, the relation of a 22e-Te_3^{4-} basic fragment to the Te_5^{4-} anions is the same as that of a 36e-Te_5^{6-} basic fragment to the anions of Re_2Te_5 or $[PPh_4]_2Se_{11}$, respectively. Interestingly, the isoelectronic 34e-$I_3Cl_2^+$[29a] cation and the 34e-I_5^+ cation[29b] are of the same shape as 34e-Te_5^{4-}, a further proof of the significance of this new conception.

Of great interest, too, is the possibility of stabilising anionic fragments by transition metals as demonstrated for a large number of chalcogenometallates[30]. Two examples concerning the stabilisation of Te_5^{4-} by gold are shown in figure 4[31,32]. Obviously the unexpected U-shape of the Te_5^{4-} unit is a result of the stabilisation by the Au^{3+} cations. The anions can be considered as η^3-ligands. Somewhat surprising, the $AuTe_5^-$ subunits of the $Au_2Te_{12}^{4-}$ anion are slightly puckered in contrast to the planar $AuTe_5^-$ subunit of the $AuTe_7^{3-}$ anion.

Structures based on T–shaped $TeTe_3^{n-}$ units

Again, as discussed for the 22e-XeF_2 basic fragment, until now no striking example of an isolated 28e-$TeTe_3^{4-}$ basic fragment, isoelectronic with T-shaped BrF_3, for instance, is known. The most simple explanation could be that a Te_4^{4-} fragment is less stable then two Te_2^{2-}-dumbbells: $Te_4^{4-} \rightarrow 2\ Te_2^{2-}$.

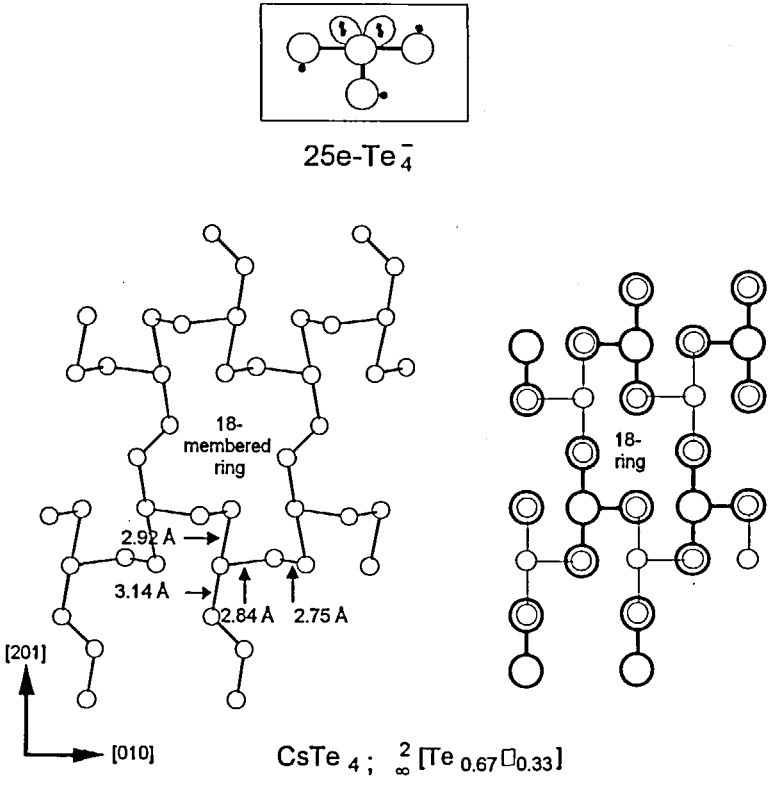

FIGURE 5 Left: section of the structure of $CsTe_4$; right: defect square double net (idealised bond parameters).

On the other hand the structure of $CsTe_4$ has been solved[33]. It consists of Cs^+ cations and 25e-Te_4^- units which need three electrons to be isoelectronic with BrF_3. As shown for M_2Te_5 (M = Rb, Cs), the lack of electrons is compensated through interconnecting these basic fragments. The structure of $CsTeSe_3$[17] can be discussed in the same manner. In both cases, puckered two-dimensional infinite layers of 18-membered chalcogene rings are observed (figure 5 left, one T-shaped unit is emphasised).

As known from many 28e-AB_3 molecules of pseudo trigonal-bipyramidal shape, the interatomic distances from the central atom to the apical ones are longer (2.92 Å, 3.14 Å) than that to the equatorial atom (2.84 Å). The bridging dumbbells again have a Te–Te distance of the magnitude of the covalent single bond distance (2.75 Å). To understand the underlying principle it is helpful to set all bond angles to 90° and make all Te–Te distances equal. It than becomes clear, that the idealised precursor structure is a defect square double net $^2_\infty[Te_{0.67}\square_{0.33}]$, which itself can be considered as stacking of two defect single square nets (figure 5, right).

Due to the argumentation stated above, the square net should be proofed to be a suitable model in order to understand the structures of further chalcogene-rich chalcogenides in a more general way. Remember, the stacking of square nets would yield the primitive cubic structure, very often proposed as a hypothetical tellurium modification with metallic behaviour. Additionally, such square nets, sometimes slightly distorted, have been found in a couple of compounds, which

structures can be derived from the Cu_2Sb type ($LnSe_n$[2,22,37-39], $LnTe_n$[1,2,36], $U_{0.9}Te_3$[34]).

STRUCTURES BASED ON SQUARE NETS

The square net is a two dimensional section of the cubic primitive structure. It is expected to be distorted or to give rise to metallic behaviour for a total of $6 \pm \delta$ valence electrons. A comprehensive discussion of the square net has already been given[35]. The principle situation is sketched in figure 6 with the Fermi level indicated for 6 electrons.

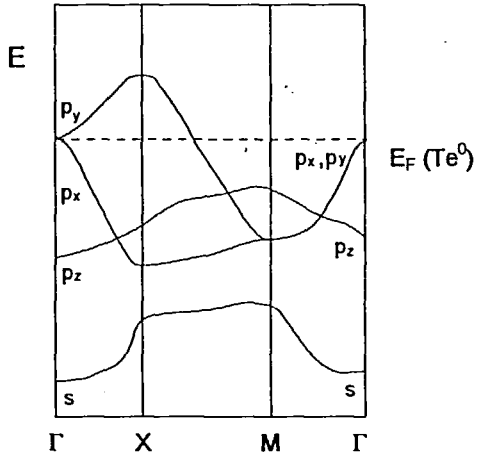

FIGURE 6 Principle trend of the highest bands of a square net. The dispersion of the bands is somewhat overemphasised (cf., for instance reference [35])

Structures based on defect square nets

A first defect square double net of tellurium has been mentioned above. As discussed, two thirds of the tellurium sites in $CsTe_4$ are occupied and one third is empty. Some tellurium atoms are 2-connected, whereas others are 3-connected (cf. Figure 5).

Additionally, some more compounds with defect square nets of different site deficencies have been published. Compounds of the general composition LnX_n (X = Se, Te; $1.7 < n < 3$) are known since the mid-sixties (table I). Reasonable structure solutions of at least the substructures have also been given[2a,36-40]. First hints of possible superstructures driven by a dumbbell separation of the chalcogene atoms of the defect square sheets became known in the mid-seventies[38]. A detailed treatment based on both, very precise X-ray determination and theoretical considerations including charge density waves and site occupation waves, has been published 1993 for the first time[22]. The model found for the defect 4^4-net of $La_{10}Se_{19}$ ($LaSe_{1.9}$) is depicted in figure 7, upper left, that found for the substructure of $RbDy_3Se_8$ ($Rb_{0.33}DySe_{2.67}$) in the upper right.A $[Te_4Te^{3-}_{4/2}]$ unit is the building block of the defect square nets of Cs_3Te_{22}[17] and Cs_4Te_{28}[17] (figure 7, bottom left). These nets are the most diluted ones so far observed: $^2_\infty[Te_{0.60}\square_{0.40}]$. The tellurium atoms are 2- and 3-connected as in $CsTe_4$. The cations occupy the largest voids of the defect square sheet. As in Tl_2GeTe_5, the Te–Te distances of the squares of the Te_8^{n-} unit, emphasised in the figure, are shorter than those between the square and its terminal tellurium atoms (3.00 Å vs. 3.08 Å). Calculations have shown that there is a tendency to lower the total

energy of a Te_8^{n-} unit by reducing the bond angle ß[20a]. This tendency seems to be suppressed in Cs_3Te_{22}. But the bond angle observed in MTe_4 (M = Nb, Ta)[3] indeed is near 70° and a similar fragment of eight tellurium atoms can be regarded as the basic building block again (figure 7, bottom right).

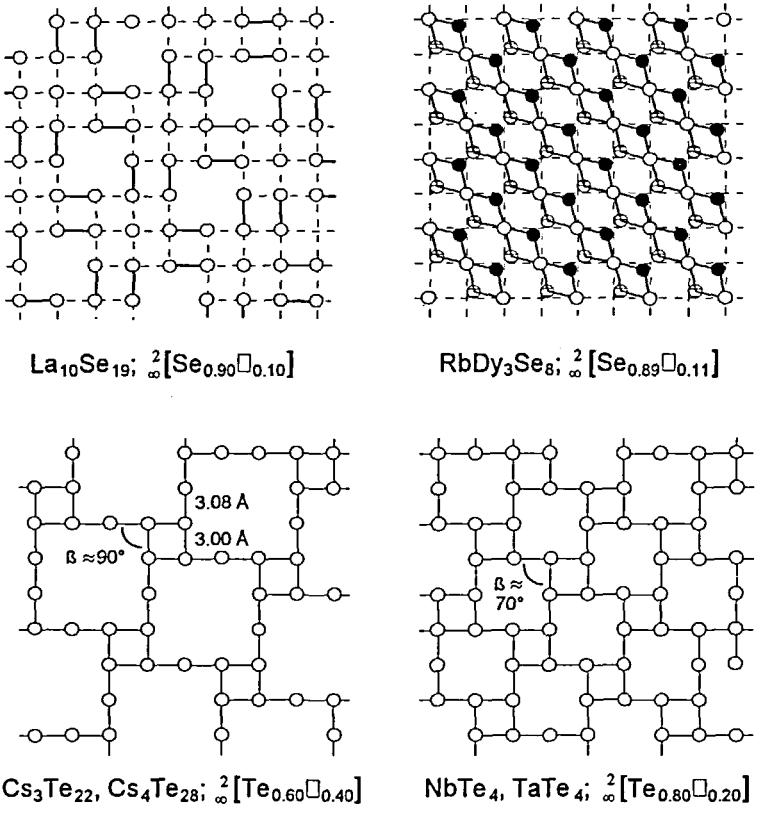

FIGURE 7 Defect chalcogene square nets; hatched: partially occupied Se(3) site of the $^2_\infty[Se_{0.89}\square_{0.11}]$ sheet of $RbDy_3Se_8$.

Structures based on full square nets

An even larger number of compounds exhibit anionic structures which can be derived from a full square (4^4) net. The binary rare earth chalcogenides LnX_n (n = 2, 2.5, 3)[2,36-39] are well known examples. If the composition of these chalcogenides precisely is 1:2, 2:5, or 1:3, respectively, no site defects should occur in their anionic structures. They are then expected to be tetragonal. Nevertheless, the structures exhibit orthorhombic or even lower symmetry only.

The $NdTe_3$ type, the most important structure type for rare earth and actinide trichalcogenides, is found to be orthorhombic, space group Cmcm. According to the cell parameters usually observed, it could be considered pseudo-tetragonal (cf., e.g., the original paper on $NdTe_3$[2]: a = b = 4.35 Å, c = 25.80 Å). Recently it has been shown for $U_{0.9}Te_3$[34], also crystallising with the $NdTe_3$ type, that the symmetry reduction from tertragonal to orthorhombic unambigiuosly originates from the kind of stacking of the building blocks of the structure instead from a distortion of the tellurium square nets. All the Te–Te distances found in these nets are 3.082(1) Å, although the tellurium atoms concerned occupy two different independent crystallographic sites. The same has been found for the substructures of $SmTe_3$ and Sm_2Te_5, the latter crystallising with a structure type closely related to the $NdTe_3$ type[40b]. As observed in $Ca_{0.67}K_4Te_3$, for instance, sometimes normal X-ray measurements cannot reveal all details of the structures. Indeed, electron diffraction investigations for a couple of $LnTe_3$ compounds (Ln = La, Sm, Gd, Tb, Dy, Ho, Er, Tm) show incommensurate superlattice reflections indicating the presence of charge density waves. This is consistent with slight atomic displacements in the

square tellurium sheets[40c]. As stated in reference [36] for the first time, metallic behaviour parallel to the sheets is observed again.

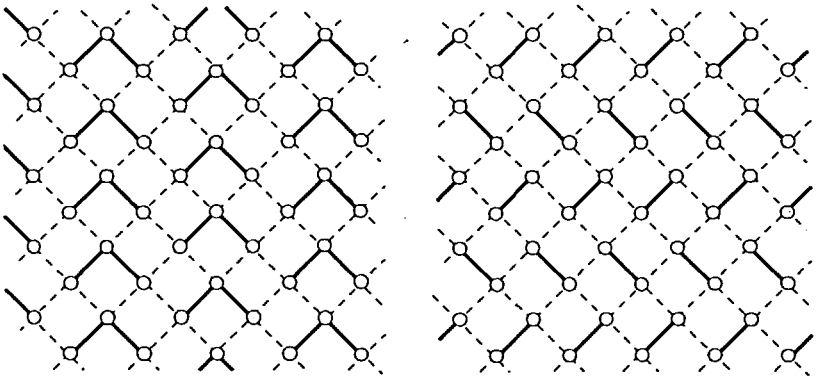

FIGURE 8 Two examples of distorted full square nets of chalcogene atoms.

The ternary compound $K_{0.33}Ba_{0.67}AgTe_2$[41] and the simple alkali metal dichalcogenide Cs_2Te_2[19b] belong to the group of compounds based on full square nets, too, showing somewhat larger deviations. Such deviations from the square net can yield bent Te_3 groups (if the bond angle is close to 90°) or lead to Te_2 dumbbells. The first pattern is found in the structure of $K_{0.33}Ba_{0.67}AgTe_2$ (figure 8, left), the latter in the structure of Cs_2Te_2 (figure 8, right). Notice the similarity of the coloumns of bent Te_3 entities in $K_{0.33}Ba_{0.67}AgTe_2$ with the anionic string of In_2Te_5 depicted in figure 3. Last, but not least, the herringbone pattern of Cs_2Te_2 resembles one of the most simple arrangements of such dumbbells. The whole structure can be

considered as a stuffed variant of the iodine structure. Nevertheless, it has been discovered just in 1996[19b].

For the largest distortions ones ends up with the $ZrSe_3$ type[3,25], which contains parallel linear chains of chalcogene atoms. In the $ZrSe_3$ type these parallel linear chains sandwich NaCl-like $^2_\infty[M^{n+}X^{2-}]$ double sheets, whereas in the $NdTe_n$ types similar $^2_\infty[M^{n+}X^{2-}]$ sheets are sandwiched between chalcogene square sheets.

STRUCTURES BASED ON THE PRIMITIVE CUBIC PATTERN

Most of the anionic fragments discussed in the previous chapters can be formally derived from sections of the cubic primitive structure after setting the bond angles to 90° and making all bond distances equal.

The compounds to be discussed in this chapter exhibit three-dimensional (defect) infinite anionic networks of chalcogene atoms. Well known examples are the compounds $AgTe_3$[8], $LiTe_3$[5], $NaTe_3$[42], and $LiSe_3$[43]. They all exhibit infinite $^3_\infty[Te^-]$ anionic defect networks of 4-connected chalcogene atoms and can be considered as 1:3 ordered variants of the cubic primitive structure (α- Po type, figure 9, left), if the two empty corners of each cube are occupied by metal atoms. $AgTe_3$ and MX_3 (M = Li, Na; X = Se, Te) are found to be rhombohedral or trigonal, respectively. This symmetry reduction from ideal cubic to trigonal or rhombohedral, parallels the situation discussed for the square sheets. Without symmetry reduction the MX_3

compounds are expected to be metals again. But conductivity measurements of trigonal distorted $NaTe_3$ reveal semiconducting behaviour, for instance (E_g: 0.7 eV; figure 9, right)[44].

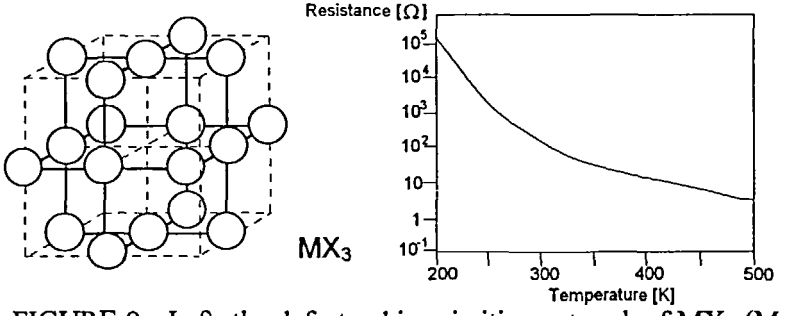

FIGURE 9 Left: the defect cubic primitive network of MX_3 (M = Ag, Li, Na; X = Se, Te). Filling the unoccupied corners of the small cubes with metal cations a 1:3 ordered variant of the α-Po type results; right: resistance vs. temperature of $NaTe_3$.

CLOSING REMARKS

Obeying the restrictions noticed (all ß = 90°; all X–X equal) the polyanions of nearly all of the compounds dicussed fit into a square network. In figure 10, some examples are given: finite molecular anions Se_{10}^{2-} found in $[Ph_3PNPPh_3]_2Se_{10}\cdot DMF$[45], one-dimensional infinite polyanions found in Cs_2Te_5[9], and two- dimensional infinite sheets observed in $RbTe_6$[17] (all shown in figure 10, left). The anionic part of Cs_2Te_{13}[17], not depicted in figure 10, is closely related to that of $RbTe_6$.

Nevertheless, one important question remains unanswered at least: The square sheeet and its three-dimensional stackings cannot be the only high symmetric net possible. Numerous substances crystalise with 3^6-, 6^3-, or 3636-nets[35]. But just in 1997 the first telluride which anionic part consists of a highly diluted 3^6-net $^2_\infty[Te_{0.24}\square_{0.76}]$ has been published ($Cr(en)_3Te_6$, figure 10, top right)[46]. One structure based on closed packed tellurium layers (···ABAB··· stacking) has already been found ($CrTe_3$, figure 10, bottom right)[47].

Besides other examples discussed in the foregoing chapters these examples illustrate our statement of the chalcogene-rich chalcogenides representing a still growing field of research in a fascinating manner.

A similar model with some further idealisations, concerning bond distances as well as bond and torsion angles, leads to an appropriate description of the classical polychalcogenides. Anions found most often in these compounds, are those, which can be derived from the

cubic primitive pattern. But due to the vast conformational variety of these anions, a concise description is much more difficult.

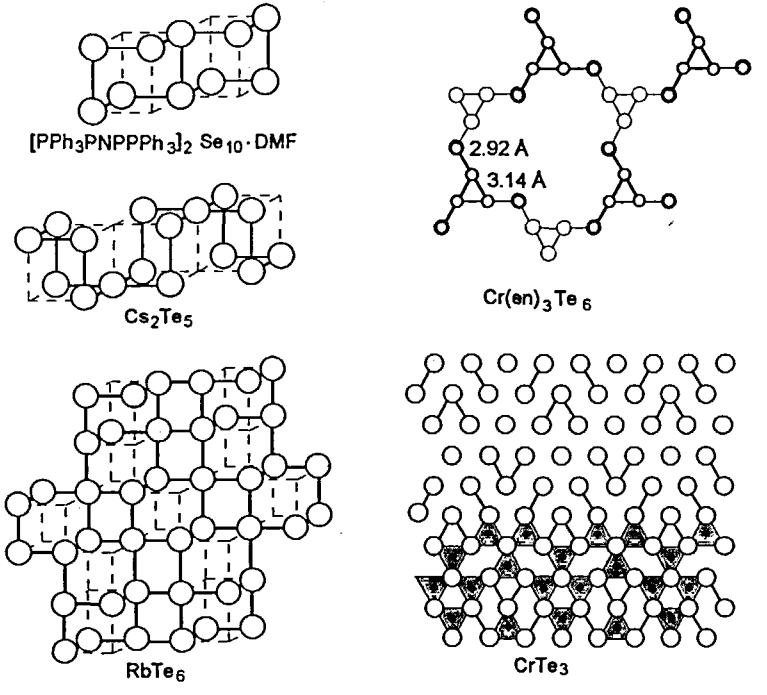

FIGURE 10 Left: cubic pattern as host structure of finite and infinite chalcogene anions after idealisation of the bonding parameters; top right: defect 3^6-nets of the anions of $Cr(en)_3Te_6$; bottom right: one distorted closed packed layer of $CrTe_3$. A few Cr atoms situated in octahedral voids are shown, too (black circles).

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