

On the Closely Related Structures of SiF₄ and CuAl₂

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It is shown that the arrays formed by the majority component atoms in the structure types of SiF₄ and CuAl₂ are topologically equivalent and can be transformed into each other by a simple distortion of their basis clusters. The geometrical flexibility of the CuAl₂ type is investigated and a structure map for the representatives of this structure type, as well as those of its derivatives BaFe₂S₄, TlSe, and U₃Si, is presented. It is suggested that the compounds BaTe₂ and SrS₂ should not be counted as representatives of the CuAl₂ type but form their own structure type. © 1997 Academic Press

STELLA QUADRANGULA AND TETRAEDERSTERN

The clusters *stella quadrangula* (SQ) and *tetraederstern* (TS) represent important building units and are especially valuable for the description of complex crystal structures of intermetallic compounds (1–5). TS was introduced in connection with the Cr₃Si structure (1) and SQ was first used to describe parts of the structures of W₃F₃C (6) and Rh₇Mg₄₄ (7). Frequently no distinction is made between them and the expression *tetraederstern* is used for both clusters types. SQ is shown in Fig. 1. It consists of a central regular tetrahedron (built of B^T atoms) with all faces capped (by the B^C atoms). This corresponds to an arrangement of four regular tetrahedra linked facially to a central one and the point group symmetry of SQ is $\bar{4}3m$ (*T_d*). The transformation from SQ to TS is depicted by Hyde and Andersson (8): The central tetrahedron of SQ is elongated along a $\bar{4}$ axis until the dihedral angle between the faces of the capping tetrahedra defining the top and bottom of the cluster becomes 180° (Fig. 1). This procedure destroys the four threefold rotation axes and four of the six mirror planes present in SQ thus reducing the point group symmetry of TS to $\bar{4}2m$ (*D_{2d}*). We define a TS as ideal when all distances between B^T and B^C atoms are equal to the two edges of the central tetrahedron perpendicular to the $\bar{4}$ axis. Related to the parent SQ cluster the only distances which are allowed to alter during the transformation to an ideal TS are the B^T–B^T distances nonperpendicular to the $\bar{4}$ axis. SQ can be inscribed in a cube. In Table 1 the resulting coordinates are compared

with those of the corresponding ideal TS with the set of short distances equal to the distances in SQ.

FROM SiF₄ TO CuAl₂

In the structure of SiF₄, F atoms form a bcc arrangement of stellae quadrangulae. The basis clusters are corner-connected in such a way that a B^C atom corresponds to a B^T atom in the neighboring cluster and vice versa (Fig. 2a). The space group symmetry of this framework is $I\bar{4}3m$ and the atomic position of the B atoms forming regular SQ is 8*c* (*x*, *x*, *x*) with *x* = 3/16. The position 6*b* (0, 1/2, 1/2) is the center of a large void defined by eight B atoms (black spheres in Fig. 2a). The Si atoms in SiF₄ are located in the central tetrahedron of SQ occupying the position 2*a* (0, 0, 0). Among further examples exhibiting this particular arrangement of SQ (9) we want to mention the structure of Tl₃VS₄ where the Tl atoms center the large voids. As a curiosity, in a recently discovered C₆₀–CS₂ clathrate the bucky balls form the SQ framework and disordered CS₂ solvent molecules are located in mutually perpendicular channels running through the center of the voids (10).

The transformation from SQ to TS in the SiF₄ structure can be described in the tetragonal *t*-subgroup $I\bar{4}2m$ (loss of the threefold rotation axes and 2/3 of the mirror planes). The position of the B atoms changes from 8*c* (3/16, 3/16, 3/16) in space group $I\bar{4}3m$ to 8*i* (3/16 – ϵ , 3/16 – ϵ , 3/16 + δ) in the lower symmetric space group (Fig. 2b). The center of the voids in the SiF₄ structure splits into two positions in $I\bar{4}2m$: position 2*b* (0, 0, 1/2) located between two basis clusters along the elongation direction (the tetragonal *c* direction) (white spheres in Fig. 2b) and position 4*c* (0, 1/2, 0) (black spheres in Fig. 2b). When *z* = 1/4 for the B atoms the transformation to TS is completed (Fig. 2b). The resulting B framework corresponds to the Al substructure in CuAl₂. Now the number of TS per unit cell appears doubled because the atomic arrangement obtained between two TS in the *c* direction is also a TS (with the position 2*b* as the center). The resulting strands of face-connected TS in this direction are shown in Fig. 2c. The voids centered at position 4*c* are transformed into square antiprisms (Fig. 2d). In

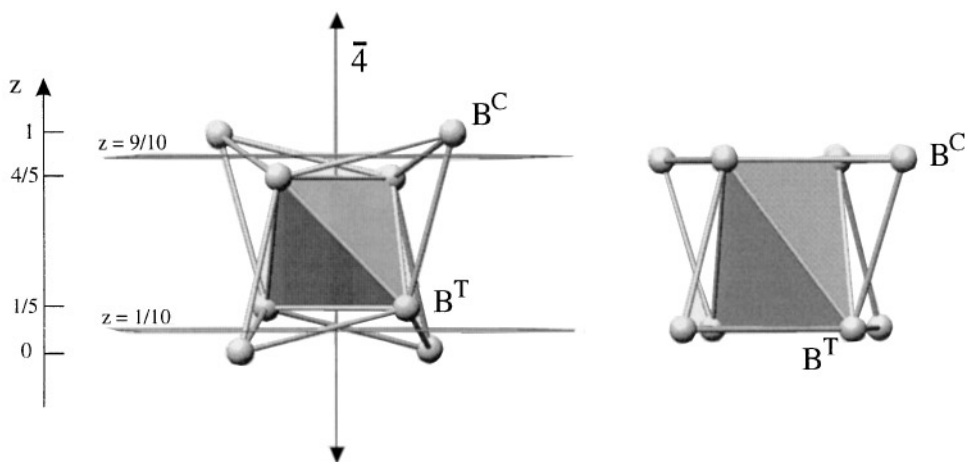


FIG. 1. The clusters stella quadrangula (left) and tetraederstern (right). A central tetrahedron formed by B^T atoms has all faces capped by B^C atoms (cf. Table 1). Figure drawn with the program COLTURE (15).

the final arrangement with ideal TS clusters the atomic parameters of the B atoms are $x = 0.18301$ and $z = 1/4$ and the c/a ratio is 0.9634. This arrangement has actually higher symmetry than $I\bar{4}2m$ because when reaching $z = 1/4$ a c -glide in the ac plane is created and the space group symmetry becomes $I4/mcm$. Figure 3 shows the relation between the space groups $I\bar{4}3m$, $I\bar{4}2m$, and $I4/mcm$. Although there is no direct group-subgroup relationship between the space groups $I\bar{4}3m$ and $I4/mcm$ the two frameworks are topologically identical as are the basis clusters SQ and TS. Besides the CuAl_2 structure (where the Cu atoms occupy the square antiprisms) this TS arrangement is for example realized in the TlSe structure with Tl atoms in the centers of the TS and the square antiprisms. The combination with only occupied tetrahedra and empty square antiprisms is not known.

TABLE 1
Coordinates of SQ and the Corresponding Idealized TS

| Atom | SQ | | | TS | | |
|-------|---------------|---------------|---------------|-------------------|-------------------|---------------------------|
| | x | y | z | x | y | z |
| B^T | $\frac{1}{5}$ | $\frac{1}{5}$ | $\frac{4}{5}$ | $\frac{1}{5}$ | $\frac{1}{5}$ | $\frac{9}{10} - \delta^a$ |
| | $\frac{4}{5}$ | $\frac{4}{5}$ | $\frac{4}{5}$ | $\frac{4}{5}$ | $\frac{4}{5}$ | $\frac{9}{10} - \delta$ |
| | $\frac{4}{5}$ | $\frac{1}{5}$ | $\frac{1}{5}$ | $\frac{4}{5}$ | $\frac{1}{5}$ | $\frac{1}{10} + \delta$ |
| | $\frac{1}{5}$ | $\frac{4}{5}$ | $\frac{1}{5}$ | $\frac{1}{5}$ | $\frac{4}{5}$ | $\frac{1}{10} + \delta$ |
| B^C | 0 | 0 | 0 | $-\varepsilon^b$ | $-\varepsilon$ | $\frac{1}{10} + \delta$ |
| | 1 | 1 | 0 | $1 + \varepsilon$ | $1 + \varepsilon$ | $\frac{1}{10} + \delta$ |
| | 1 | 0 | 1 | $1 + \varepsilon$ | $-\varepsilon$ | $\frac{9}{10} - \delta$ |
| | 0 | 1 | 1 | $-\varepsilon$ | $1 + \varepsilon$ | $\frac{9}{10} - \delta$ |

^a $\delta \approx 0.00517$.

^b $\varepsilon \approx 0.01963$.

STRUCTURAL FLEXIBILITY OF THE CuAl_2 TYPE

Two parameters c/a ratio and x value control the distortion of the TS framework. This framework is determined by four different distances which may be divided into two sets: the distances between two atoms B^T and between two atoms B^T and B^C at different heights in the c direction ($d_{O(B^T B^T)}$ and $d_{O(B^T B^C)}$, Fig. 2c) and the distances between the same pairs of atoms forming a plane net ($d_{I(B^T B^T)}$ and $d_{I(B^T B^C)}$, Fig. 2d). Table 2 lists the equations of these distances for variable values of x and the c/a ratio. The condition for a framework consisting of ideal TS is $d_{I(B^T B^C)} = d_{I(B^T B^T)} = d_{O(B^T B^C)}$. Figure 4 shows the result of a variation of x , and the situation for $x = 0.18301$, corresponding to an ideal TS, is displayed in Fig. 4c. Focusing on the square antiprism, the rotation angle ϕ of the pair of opposite faces follows the relation $\phi = \arctan(1 - 4x)$ (shown in Fig. 5a) yielding $\phi = 30^\circ$ for $x = 0.18301$. For $x \rightarrow 1/4$ TS cluster and square antiprism transform to cubes ($\phi \rightarrow 0^\circ$) and the TS framework to a simple cubic array (Fig. 4d), a relation already been pointed out by Hyde and Andersson (11). When the x value is decreased to 0.14645 one obtains at $c/a = 0.9102$ a TS framework with regular antiprisms ($\phi = 45^\circ$) (Fig. 4b) and at even smaller values of x dumbbells of B atoms appear because $d_{I(B^T B^T)}$ diminishes (Fig. 4a). In Fig. 5b the variation of d_I as a function of x and in Fig. 5c the variation of d_O as a function of x and c/a is summarized. In the diagram of Fig. 5d the borderlines indicating idealized conditions are drawn.

A GEOMETRICAL STRUCTURE MAP

Which ranges of the c/a ratio and the x values are actually realized in binary and ternary compounds exhibiting the

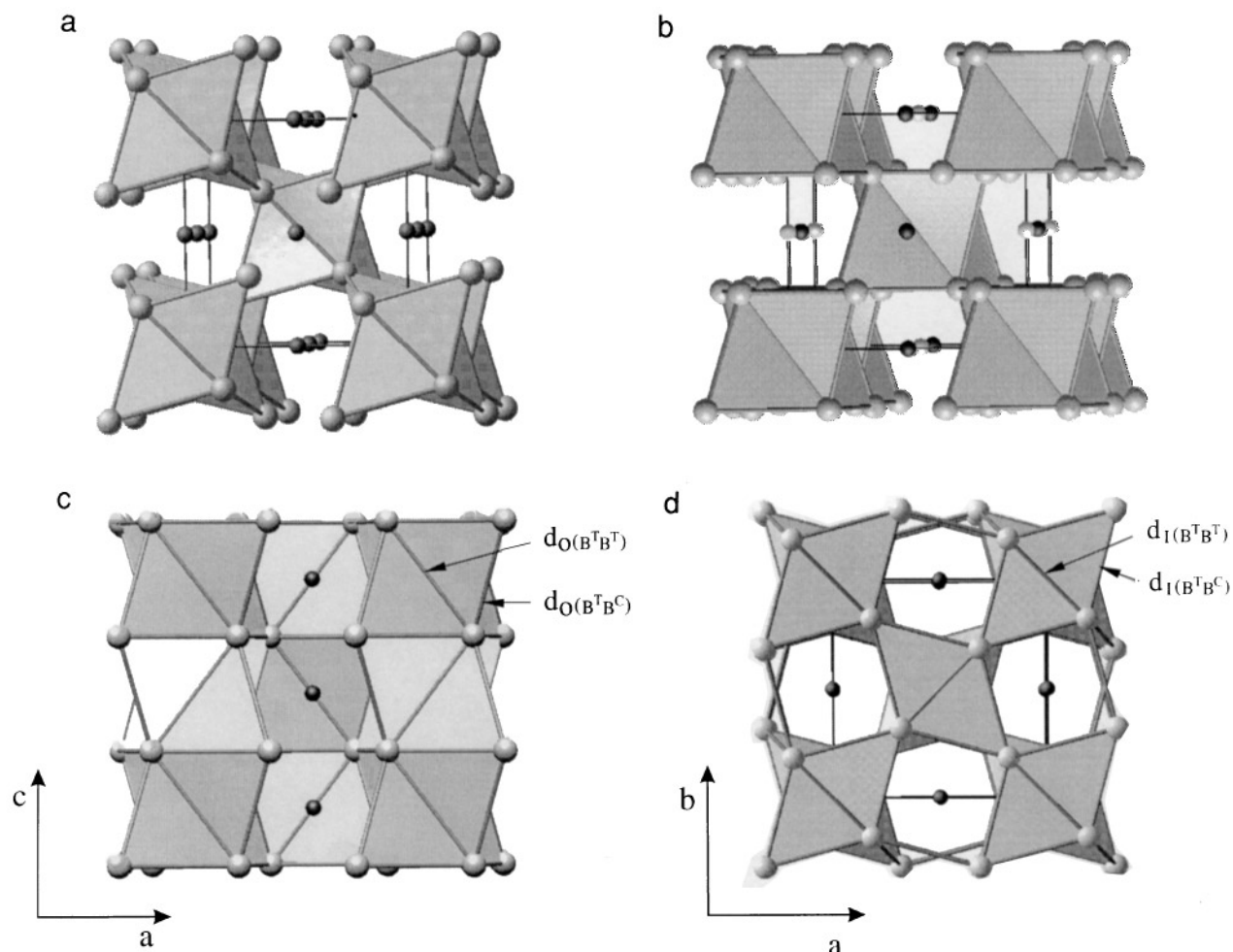
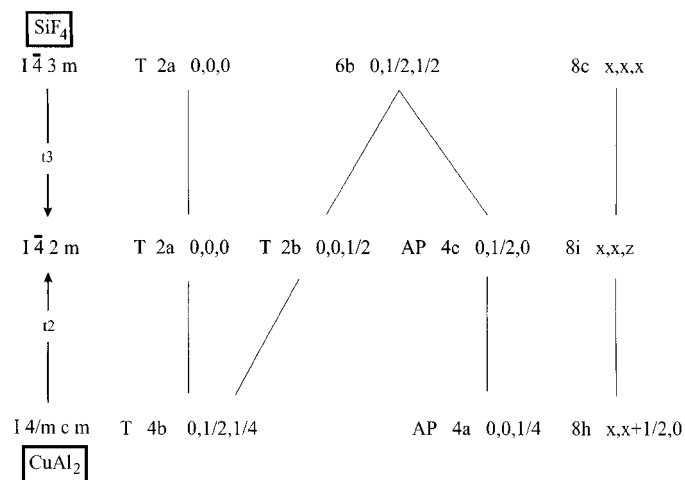


FIG. 2. (a) The arrangement of stellae quadrangulae in the structure of SiF₄. The dark spheres center the voids at position $6b$ ($0, 1/2, 1/2$). (b) The arrangement of tetraedersterns obtained by the distortion of the stellae quadrangulae clusters in SiF₄. Note that the void position in SiF₄ splits into two crystallographically different sites (light and dark spheres). The structure of CuAl₂: (010) projection (c) and (001) projection (d). Figure drawn with the program COLTURE (15).



discussed TS framework and occupied tetrahedra and square antiprisms? The inspection of the database ICSD (12) and Pearson's Handbook of Crystallographic Data for Intermetallic Phases (13) yielded 85 compounds with space group symmetry $I4/mcm$ and occupied Wyckoff positions $8h$, $4a$, and $4b$ (14). They are grouped in four different structure types: The CuAl₂ type (Al in $8h$, Cu in $4a$), the TlSe type (Se in $8h$, Tl in $4a$ and $4b$), the BaFe₂S₄ type (S in $8h$, Fe in $4b$, and Ba in half occupied $4a$), and the U₃Si type (U in $8h$

FIG. 3. Symmetry relationship between the SiF₄ and the CuAl₂ structure. The space groups $I\bar{4}3m$ and $I4/mcm$ are both minimal lattice-equivalent supergroups of $I\bar{4}2m$. Sites centering a tetrahedron are marked with T, sites centering a square antiprism with AP. Note the origin shift when going from $I4/mcm$ to $I\bar{4}2m$.

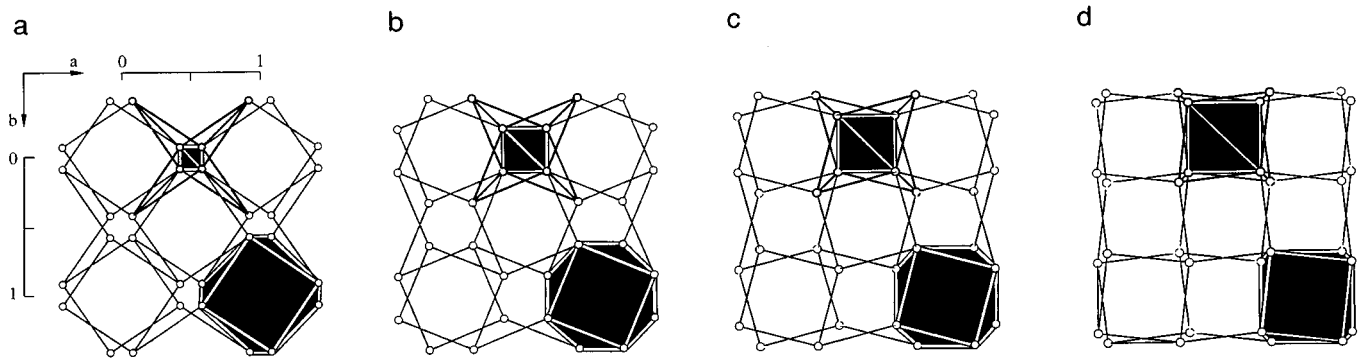


FIG. 4. Different shapes of the CuAl_2 -TS framework when varying the atomic x parameter. (a) $x = 0.08$ (framework with B_2 dumbbells in the ab plane); (b) $x = 0.14645$ (framework with regular antiprisms); (c) $x = 0.18301$ (framework with idealized TS); (d) $x = 0.225$ (framework close to a simple cubic arrangement).

and $4a$, Si in 4b). In the structure map of Fig. 6a the compounds segregate into three different regions. (1) The vast majority has a c/a ratio between 0.7 and 0.9 and an x value

between 0.15 and 0.19. (2) The small group of U_3Si type compounds has large values for x and the c/a ratio. (3) The compounds BaTe_2 and SrS_2 have small x values and a c/a

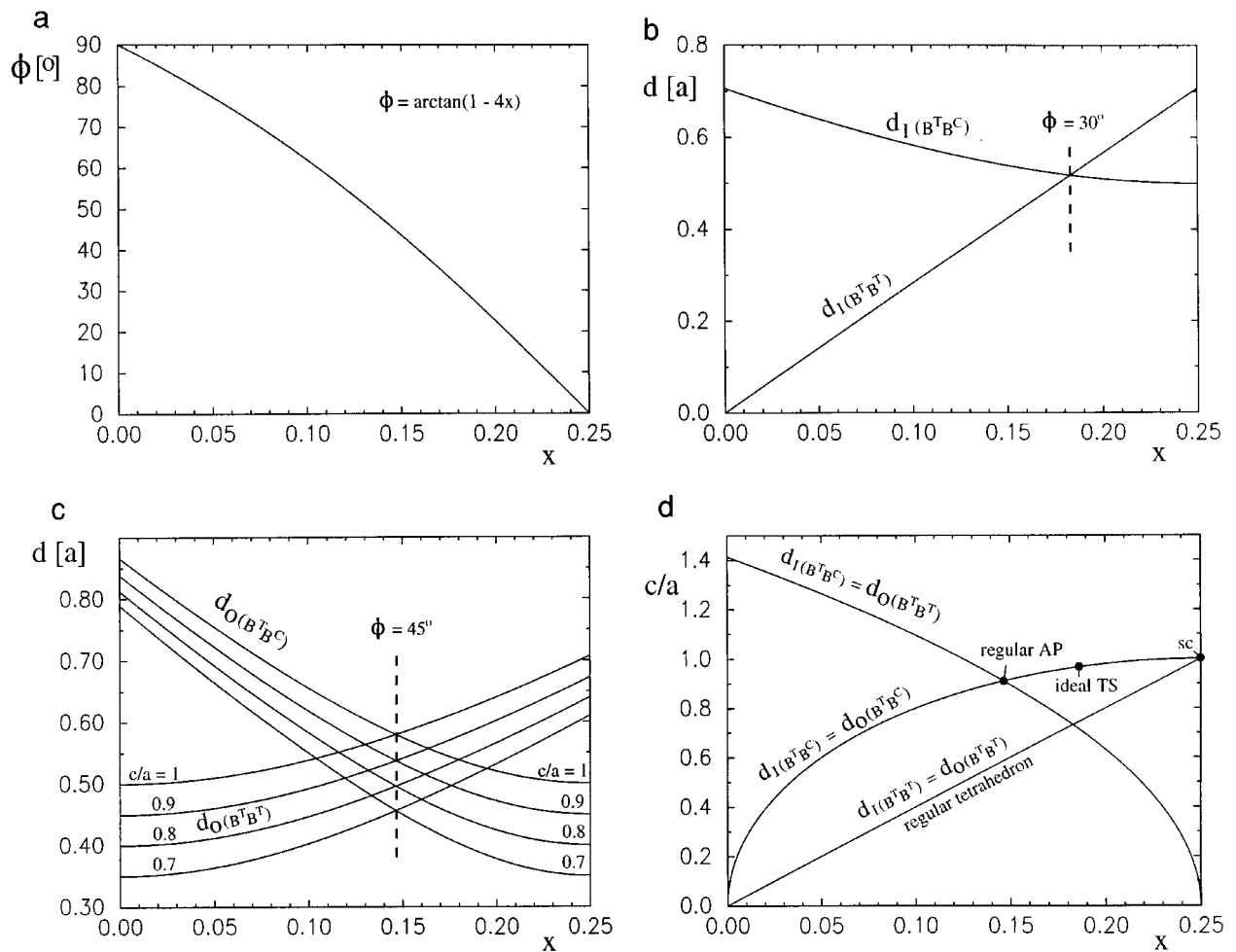


FIG. 5. Geometrical flexibility of the TS framework in CuAl_2 . (a) Relation between the rotation angle ϕ of the pair of opposite faces in the square antiprisms and the atomic x parameter. (b) Variation of the distances d_l perpendicular to the c direction as a function of x . (c) Variation of d_0 as a function of x and c/a . (d) Borderlines of idealized conditions.

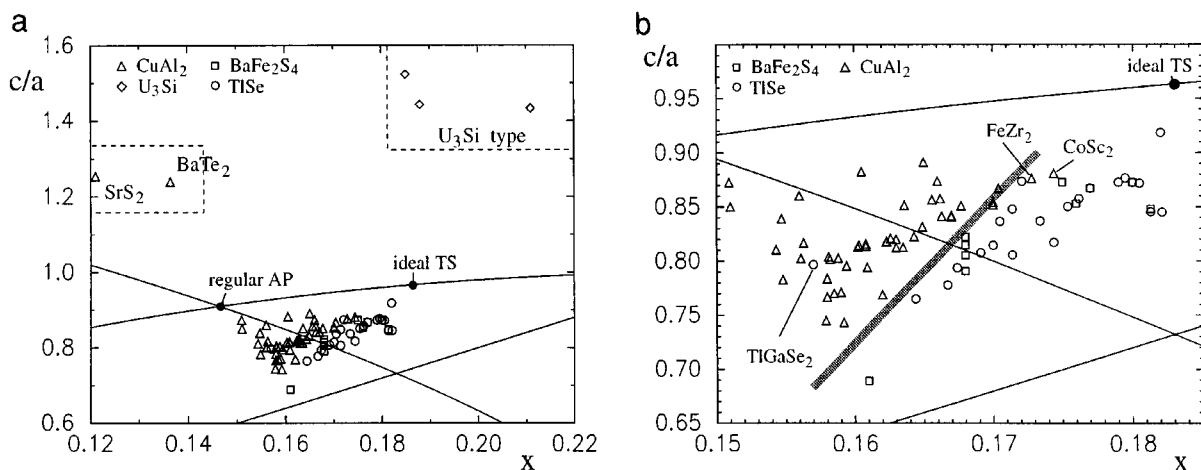


FIG. 6. (a) Geometrical structure map of compounds with the CuAl_2 -TS framework and occupied square antiprisms of antiprisms or tetrahedra. (b) Enlarged section of (a). The lines of idealized conditions (Fig. 5d) are included.

ratio between 1.2 and 1.3. They are usually classified as representatives of the CuAl_2 type. Apparently they would be better described in a separate structure type as the representatives for the U_3Si type are, thus accounting for the other extreme of TS distortion, namely the formation of isolated B_2 dumbbells (cf Fig. 4). A closer look at the compounds in region 1 reveals that it is indeed possible to separate the representatives with the CuAl_2 type (empty tetrahedra) from those with the TiSe and BaFe_2S_4 type (occupied tetrahedra) (Fig. 6b). The latter have in general higher x values which enlarge the tetrahedra and diminish the square antiprisms. In both groups there is a tendency to enlarge the c/a ratio with increasing x thus compensating for the shrinkage of the square antiprisms in the ab plane by an elongation in c direction. Some compounds with the CuAl_2 structure almost fulfill the condition for regular square antiprisms.

TABLE 2
Distances in the TS Framework of CuAl_2 Dependent on the Atomic x Parameter (All) and the c/a Ratio (Only d_0)

| d [a] | $0 \leq x \leq \frac{1}{4}$ |
|------------------|--|
| $d_{I(B^i B^j)}$ | $2\sqrt{2}x$ |
| $d_{I(B^i B^e)}$ | $\sqrt{4x^2 - 2x + \frac{1}{2}}$ |
| $d_{O(B^i B^j)}$ | $\sqrt{4x^2 + \frac{1}{4}(c/a)^2}$ |
| $d_{O(B^i B^e)}$ | $\sqrt{8^2 - 4x + \frac{1}{2} + \frac{1}{4}(c/a)^2}$ |

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