

Some Structures Containing *Stellae Quadrangulae*

BY HARRY NYMAN

Research School of Chemistry, Australian National University, PO Box 4, Canberra, ACT 2600, Australia

(Received 18 October 1982; accepted 1 April 1983)

Abstract

The structures of Tl_3VS_4 , $Ge_8Na_6Pt_8$, Na_4SnS_4 , gehlenite, $Li_6Si_2O_7$, NaPb and Na_2S_4 are described by using *stellae quadrangulae* as binding elements.

Introduction

The usefulness of *stellae quadrangulae* (SQ's) in describing crystal structures (even complicated ones), was shown in some earlier papers (Nyman, Andersson, Hyde & O'Keeffe, 1978; Nyman & Andersson, 1979*a,b*). There we defined an SQ as a tetrahedron with a cap on every face or a central tetrahedron sharing all faces with tetrahedra. We also described the logical extension of an SQ (seen as a small cluster) to be triangular caps on the edges of the tetrahedra, the final cluster being a γ -brass cluster. Here we present some more examples of structures containing SQ's.

Tl_3VS_4 , $Ge_8Na_6Pt_8$ and Na_4SnS_4 : structures related to the SiF_4 -type structure

One of the simplest structures containing SQ's is probably the structure of SiF_4 (Nyman & Andersson, 1979*b*). The structure is cubic with a simple corner-connected framework of SiF_8 SQ's, Fig. 1.

The structure of Tl_3VS_4 (Crevecoeur, 1964) and the isostructural K_3SbS_4 , Na_3SbS_4 , $(NH_4)_3SbS_4$ have the same arrangement of SQ's but here the SQ's are capped. The central VS_4 tetrahedron has a Tl atom

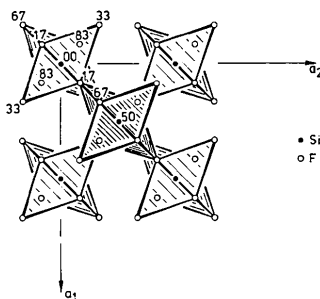


Fig. 1. The structure of SiF_4 projected along $[001]$.

capping every edge and each cap is common to two SQ's, Fig. 2. The same type of 'cluster' is found in the structure of Th_6Mn_{23} (Nyman & Andersson, 1979*a*), although the connection of the 'clusters' is different. The coordination polyhedron around Tl is a distorted bisdisphenoid.

The Na_6Ge_8 part of the structure of $Ge_8Na_6Pt_8$ (Thronberens & Schuster, 1979) corresponds exactly to the Tl_3S_4 part of Tl_3VS_4 . However, instead of having the central tetrahedron of an SQ occupied, as in Tl_3VS_4 , the four capping tetrahedra are occupied (by Pt atoms) in $Ge_8Na_6Pt_8$, Fig. 3. That is: $Tl_3VS_4 \cong Na_3(Pt_4)Ge_4 = \frac{1}{2}Na_6Pt_8Ge_8$.

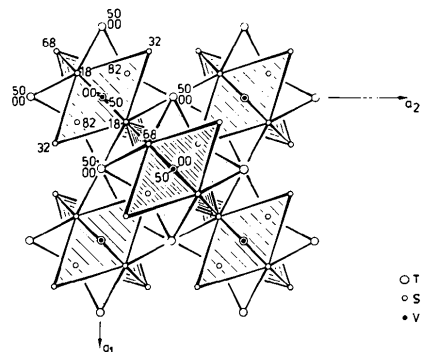


Fig. 2. The structure of Tl_3VS_4 projected along $[001]$. Triangular caps are dotted.

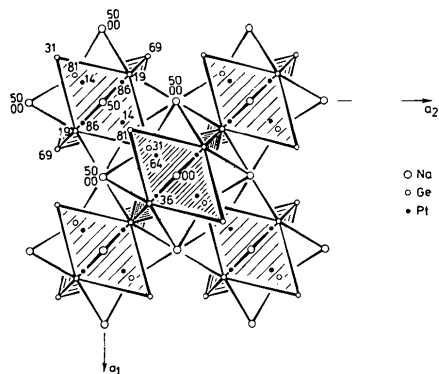


Fig. 3. The structure of $Ge_8Na_6Pt_8$ projected along $[001]$. Triangular caps are dotted.

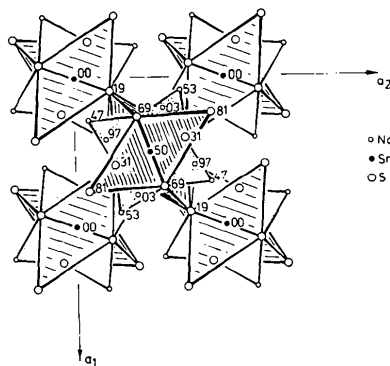


Fig. 4. The structure of Na_4SnS_4 projected along $[001]$. Triangular caps are dotted.

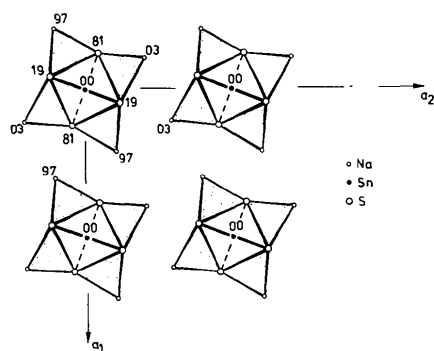


Fig. 5. Part of the structure of Na_4SnS_4 , showing the rotation of the central tetrahedra with its triangular caps (dotted).

Fig. 4 shows a projection of the structure of Na_4SnS_4 (Jumas, Vermot-Gaud-Daniel & Philippot, 1973) along its tetragonal c axis. The arrangement of corner-connected SQ's (here distorted) is the same as in Tl_3VS_4 . However, in Na_4SnS_4 each SQ has only four triangular caps all belonging to one SQ only, and all perpendicular to the c axis. To make room for two capping atoms between the SQ's instead of one common cap, as in Tl_3VS_4 , the central tetrahedron (of the SQ) with its caps has to rotate around an axis parallel to c . This rotation, shown in Fig. 5, is $\sim 25^\circ$ in Na_4SnS_4 , and is the cause for the distortion of the SQ's.

Gehlenite and $\text{Li}_6\text{Si}_2\text{O}_7$; structures related to the Cr_3Si type structure

Gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (Louisnathan, 1971), which belongs to the melilite family of structures, is also built of SQ's. The connectivity of the SQ's, Fig. 6, differs from that in the previously mentioned structures (although corner-connection) and, if fully opened up, has some resemblance to the structure of Cr_3Si

(Andersson, 1978). The deviation from the Cr_3Si structure (rotation of the Al-centred SQ's around axes parallel to the c axis) is caused by SiAlO_7 pairs of tetrahedra sharing edges with the SQ's. One such pair of tetrahedra is indicated in the central part of Fig. 6. The layers of SQ's and tetrahedra are separated by layers of Ca atoms, each coordinated to eight O atoms in the shape of a heavily distorted square antiprism as depicted in the right part of Fig. 6.

An almost identical array of SQ's is found in the structure of $\text{Li}_6\text{Si}_2\text{O}_7$ (Völlenkne, Wittmann & Nowotny, 1969), Fig. 7. However, here the SQ's are not centred by one atom, as in gehlenite, but by four (Li), cf. Tl_3VS_4 and $\text{Ge}_8\text{Na}_6\text{Pt}_8$ above. This forces the Si_2O_7 pairs of tetrahedra to move out of the SQ layers and they are here separating these layers by corner-connection, as shown in the central part of Fig. 7. The right part of Fig. 7 shows the O coordination around the remaining Li atoms. The coordination polyhedron is again a distorted square antiprism, but the Li atoms are off-centre and close to one of the four-sided faces. Also, the antiprisms are at the same level as the SQ layers and not between them, as in gehlenite.

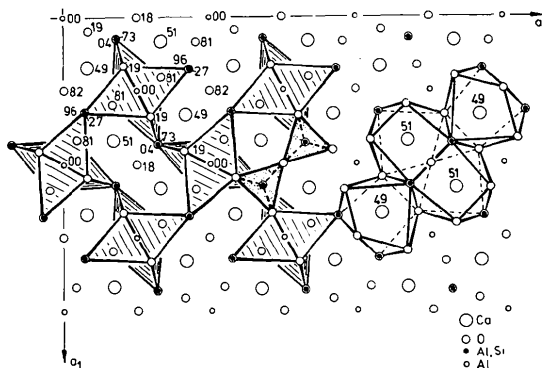


Fig. 6. The structure of gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) projected along the tetragonal axis. For clarity only one SiAlO_7 pair of tetrahedra is indicated (dotted).

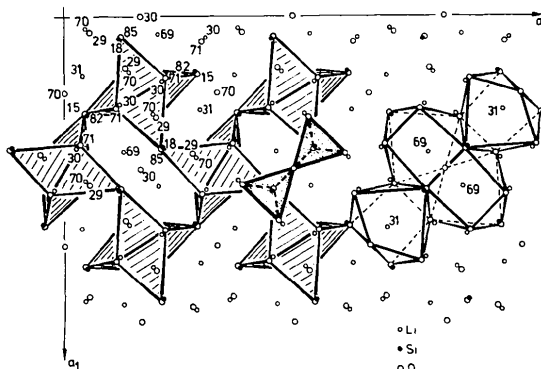


Fig. 7. The structure of $\text{Li}_6\text{Si}_2\text{O}_7$ projected along the tetragonal axis. Only one Si_2O_7 pair of tetrahedra is depicted (dotted).

NaPb and Na₂S₄; structures related to the W₃Fe₃C-type structure

A third way of corner-connecting SQ's is shown in the structure of NaPb (Marsh & Shoemaker, 1953), Fig. 8. A Pb₄ tetrahedron with an Na atom capping every face creates an SQ. A second set of Na atoms put four triangular caps onto the SQ's. As in the structure of Na₄SnS₄, the triangular caps are perpendicular to the tetragonal *c* axis. The complete structure of NaPb consists of two identical interpenetrating frameworks of corner-connected SQ's. The two frameworks are connected to each other by the triangular caps, as can be seen in Fig. 8, where the two SQ's to the right on the bottom row belong to the second framework.

A comparison with the Fe-atom array in the structure of W₃Fe₃C (Nyman *et al.*, 1978), Fig. 9, shows that the SQ framework of NaPb is a collapsed 'Fe-atom array', the collapse again obtained by rotating the SQ's around axes parallel to the tetragonal *c* axis.

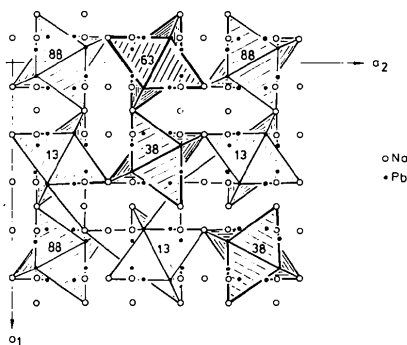


Fig. 8. The structure of NaPb projected along the tetragonal axis. Heights, in hundredths of *c*, indicate the centres of the SQ's. All SQ's, except the two to the right on the bottom row, belong to one SQ framework.

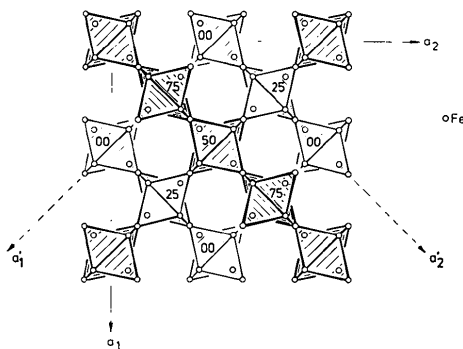


Fig. 9. The Fe part of the structure of W₃Fe₃C. The figures show the heights of the centres of the SQ's. A body-centred tetragonal unit cell is indicated with primed letters.

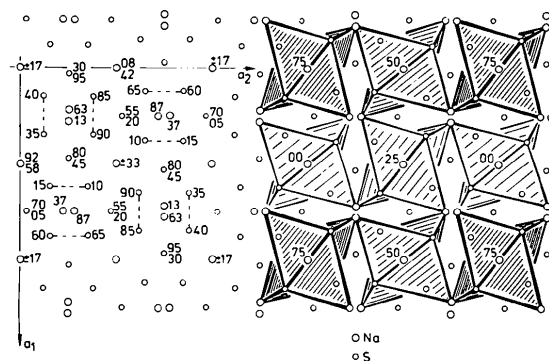


Fig. 10. The structure of Na₂S₄ projected along the tetragonal axis. Heights shown in the right part are the centres of the SQ's which are unoccupied.

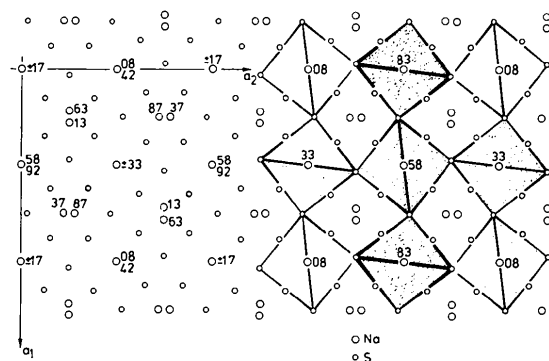


Fig. 11. One framework of corner-connected NaS₄ tetrahedra in the Na₂S₄ structure. For remaining heights of atoms, see Fig. 10.

A similar framework of SQ's, although more collapsed, is found in the structure of Na₂S₄ (Tegman, 1973), Fig. 10. The rotation of the S₄Na₄ SQ's creates some short S—S distances (indicated by hatched lines in the left part of Fig. 10) which is a common feature of polysulphides. This framework of SQ's is interpenetrated by two identical frameworks of corner-connected NaS₄ tetrahedra.

Such a tetrahedral framework, as shown in Fig. 11, has a high-cristobalite-type structure (O'Keeffe & Hyde, 1976) and is not connected to either the SQ framework or the second framework of tetrahedra.

Concluding remarks

By using SQ's it is possible to describe the structures mentioned here as frameworks instead of isolated groups of atoms. The geometrical relationships to other structures are thereby made clearer. The method also shows the similarity (geometrically) between structures with different types of bonding, *i.e.* metallic and ionic compounds.

References

- ANDERSSON, S. (1978). *J. Solid State Chem.* **23**, 191–204.
 CREVECOEUR, C. (1964). *Acta Cryst.* **17**, 757.
 JUMAS, J. C., VERMOT-GAUD-DANIEL, F. & PHILIPPOT, E. (1973). *Cryst. Struct. Commun.* **2**, 157–158.
 LOUISNATHAN, S. J. (1971). *Can. Mineral.* **10**, 822–837.
 MARSH, R. E. & SHOEMAKER, D. P. (1953). *Acta Cryst.* **6**, 197–205.
 NYMAN, H. & ANDERSSON, S. (1979a). *Acta Cryst.* **A35**, 580–583.
 NYMAN, H. & ANDERSSON, S. (1979b). *Acta Cryst.* **A35**, 934–937.
 NYMAN, H., ANDERSSON, S., HYDE, B. G. & O'KEEFFE, M. (1978). *J. Solid State Chem.* **26**, 123–131.
 O'KEEFFE, M. & HYDE, B. G. (1976). *Acta Cryst.* **B32**, 2923–2936.
 TEGMAN, R. (1973). *Acta Cryst.* **B29**, 1463–1469.
 THRONBERENS, W. & SCHUSTER, H.-U. (1979). *Z. Naturforsch. Teil B*, **34**, 781–783.
 VÖLLENKLE, H., WITTMANN, A. & NOWOTNY, H. (1969). *Monatsh. Chem.* **100**, 295–303.

Acta Cryst. (1983). **B39**, 532–535

Metal Ordering in $(\text{Fe,V})_3\text{S}_4$

BY HIROMOTO NAKAZAWA

National Institute for Research in Inorganic Materials, Namiki 1, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

KATSUHIRO TSUKIMURA

Geological Survey of Japan, Namiki 3, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

HISAKO HIRAI

Department of Geosciences, University of Tsukuba, Tennodai, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

AND HIROAKI WADA

National Institute for Research in Inorganic Materials, Namiki 1, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

(Received 15 December 1982; accepted 19 April 1983)

Abstract

The ordered arrangement of metals in $(\text{Fe,V})_3\text{S}_4$ was determined by means of powder X-ray diffraction employing the anomalous dispersion of Cr $K\alpha$ radiation for V and Fe atoms, although both atoms have similar atomic numbers. By comparison of the observed and calculated structure factors of FeV_2S_4 and $(\text{Fe}_2\text{V})_{2.88}\text{S}_4$ for Cr $K\alpha$, Fe $K\alpha$ and Cu $K\alpha$ radiations, it was concluded that Fe atoms occupy preferentially the $M(1)$ site in the metal layer with vacancies, indicating that Fe atoms have a relatively stronger tendency to have neighbouring metal atoms along the c axis than do V atoms.

Introduction

The transition-metal sulphides, commonly having the NiAs-type structure at high temperatures, undergo one or a series of phase transformations in which their ordered arrangements of vacancies change with decreasing temperature. V_3S_4 is such an example and has a supercell of $\sqrt{3}A \times A \times 2C$, where A and C are the

cell edges of the NiAs-type fundamental cell. Its structure is the Cr_3S_4 type at room temperature, consisting of two alternate metal layers with and without vacancies and of approximately hexagonal close-packed S layers (Fig. 1) (Kawada, Nakano-Onoda,

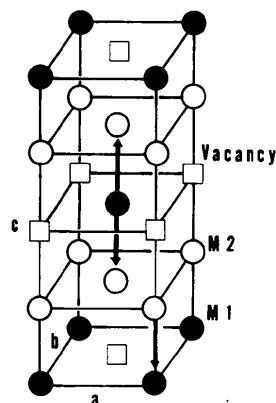


Fig. 1. Sublattice of metal atoms, $M(1)$ and $M(2)$, and vacancies in the $(\text{Fe,V})_3\text{S}_4$ structure. Arrows demonstrate the number of neighbouring metals around the $M(1)$ and $M(2)$ sites along the c axis.