

## Preparation and crystal structure of $\text{Na}_4\text{Cu}_2\text{S}_3$ , a thiocuprate with discrete anions

Kurt O. Klepp, Martin Sing and Herbert Boller

Department of General and Inorganic Chemistry, University of Linz,  
Altenbergerstrasse 69, A-4040 Linz (Austria)

(Received October 21, 1991; in final form November 14, 1991)

### Abstract

Transparent pale yellow crystals of  $\text{Na}_4\text{Cu}_2\text{S}_3$  were obtained from the melt of a corresponding mixture of the binary sulphides.  $\text{Na}_4\text{Cu}_2\text{S}_3$  is tetragonal, space group  $I4_1/a$  with  $a = 9.468(1)$  Å,  $c = 36.64(2)$  Å and  $Z = 16$ . The crystal structure was determined from four-circle diffractometer data and refined to a conventional  $R$  of 0.021 for 1682 observed reflections with  $F_o^2 > 3\sigma(F_o^2)$  and 83 variables.

An outstanding feature of  $\text{Na}_4\text{Cu}_2\text{S}_3$  is the formation of discrete V-shaped thiocuprate anions  $[\text{S}-\text{Cu}-\text{S}-\text{Cu}-\text{S}]^{4-}$ , with copper in an almost linear coordination by sulphur. The bond lengths ( $d_{\text{Cu}-\text{S}} = 2.15$  Å) and angles are in good agreement with those of the infinite anionic chains of  $\text{KCuS}$ .

The crystal structure is based on a cubic close-packed arrangement of sulphur atoms with sodium in the centres of the tetrahedral voids, while copper atoms are shifted from the centres towards one of the edges in order to attain a linear co-ordination.

### 1. Introduction

Despite the fact that the formation of low melting sodium thiocuprates used to play an important role in the metallurgical refining of Cu–Ni sulphide mixtures (Orford process), information on the intermediate phases in the ternary system Na–Cu–S is rather scarce. Thus, until recently, only three sodium thiocuprates have been structurally characterized: the mixed valent compound  $\text{Na}_3\text{Cu}_4\text{S}_4$  [1], which has an interesting pseudo-one-dimensional structure; the layered compound  $\text{Na}_2\text{Cu}_4\text{S}_3$  [2], isostructural with  $\text{Cs}_2\text{Ag}_4\text{S}_3$  [3]; the compound  $\text{NaCu}_5\text{S}_3$  [4], which had been obtained by hydrothermal synthesis.

In previous literature claims have been made for the existence of the compounds  $\text{Na}_2\text{Cu}_3\text{S}_3$  [5],  $\text{Na}_2\text{Cu}_8\text{S}_5$  [6] and  $\text{NaCuS}$  [7, 8]. However, these findings were not corroborated.

In the course of a reinvestigation of the Na–Cu–S system, which had been stimulated by these discrepancies, we found no indications of the formation of the equiatomic ternary compound  $\text{NaCuS}$ . In the cation-rich

---

\*Correspondence to: Professor Kurt O. Klepp, Department of General and Inorganic Chemistry, University of Linz, Altenbergerstrasse 69, A-4040 Linz, Austria.

region of the section  $\text{Na}_2\text{S}-\text{Cu}_2\text{S}$  we were, however, able to detect a new intermediate phase,  $\text{Na}_4\text{Cu}_2\text{S}_3$ , the preparation and structure of which will be reported in the following section.

## 2. Experimental details

The starting materials for the preparation of  $\text{Na}_4\text{Cu}_2\text{S}_3$  were the binary compounds  $\text{Na}_2\text{S}$  and  $\text{Cu}_2\text{S}$ . For the preparation of the alkali sulphide, a freshly prepared solution of  $\text{NaHS}$  was reacted with an equimolar amount of  $\text{NaOH}$ . The reaction mixture was cooled, the precipitated compound  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  isolated and recrystallized twice under an oxygen-free atmosphere. The nonahydrate was decomposed in a desiccator and the residual water was removed by the careful evacuation of the product by slowly raising the temperature from ambient to  $280^\circ\text{C}$ .  $\text{Cu}_2\text{S}$  was obtained by the reaction of an intimate mixture of freshly reduced copper powder and sulphur (both of 99.99% purity). The product was then annealed at  $300^\circ\text{C}$  for several days. Both starting materials (as was shown by their Guinier diagrams) were roentgenographically pure.

For the preparation of  $\text{Na}_4\text{Cu}_2\text{S}_3$ , the two binary sulphides were mixed in the corresponding molar ratio and sealed into a silica tube whilst maintaining a vacuum of  $10^{-2}$  Pa. The sample was heated to 1070 K (when the product became molten) and then allowed to cool to ambient temperature with a controlled cooling rate of  $4.6^\circ\text{C h}^{-1}$ . The microscopic investigation of the crushed sample performed under inert conditions revealed transparent pale yellow crystals of  $\text{Na}_4\text{Cu}_2\text{S}_3$  to be the major component. The compound is extremely sensitive to both air and moisture.

## 3. Structure determination

For the determination of the crystal structure, an irregularly shaped single crystal with the approximate dimensions  $0.125 \times 0.10 \times 0.075 \text{ mm}^3$  was selected, sealed into a thin-walled glass capillary and transferred to a four-circle diffractometer (Enraf-Nonius CAD4). Preliminary investigations performed on the diffractometer revealed tetragonal symmetry (Laue class,  $4/m$ ). From the systematic absences ( $hkl$ ;  $h+k+l \neq 2n$ ;  $hk0$ ,  $h \neq 2n$ ;  $00l$ ,  $l \neq 4n$ ) the space group was unambiguously identified as  $I4_1/a$  (No. 88). Precise cell dimensions were obtained by least-squares refinement of the angular positions of 24 well-centred high-angle reflections ( $30^\circ > 2\theta > 40^\circ$ ). The data collection was carried out at a controlled temperature of  $21(1)^\circ\text{C}$  using graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). The intensity data were determined with conventional background peak background (BPB scans) over one octant of the reflection sphere in the range  $2^\circ < 2\theta < 56^\circ$  ( $\omega-2\theta$  scan mode; scan width,  $0.80^\circ + 0.35^\circ \tan \theta$ ; maximum scan time, 120 s). The periodic determination of three control reflections, well distributed

in reciprocal space, revealed no significant changes in the diffraction power of the crystal during the time of the data collection. A total of 2260 reflections was measured. The final data set obtained after averaging the symmetry equivalent reflections ( $R_{\text{int}}=0.014$ ) and the elimination of the systematic absences comprised 1972 reflections, from which 1682 with  $F_o^2 > 3\sigma(F_o^2)$  were considered as significant.

The crystal structure was solved by direct methods (MULTAN 82 [9]). An  $E$ -map calculated from a phase set of 191  $E$ -values greater than 1.65 (2910 triplet relations) revealed the Cu-S partial structure. The sodium atoms were located in a series of subsequent difference Fourier syntheses. Least-squares refinements of the complete structure with isotropic temperature factors and unit weights led to a conventional  $R$  value of 0.052. The refinements with anisotropic temperature factors and an optimized weighting scheme finally converged at  $R=0.021$  ( $R_w=0.021$ ). A final difference Fourier map was featureless. Further details on the refinement, cell dimensions and other crystallographically relevant data are summarized in Table 1.

The atomic scattering factors for the neutral atoms and anomalous dispersion corrections were taken from the International Table for X-ray Crystallography [10]. The absorption effects were not accounted for. All the calculations were performed on a DEC-MicroVAX 3520 computer using programs of the Enraf-Nonius crystallographic software package [11]. The atomic co-ordinates and equivalent isotropic thermal parameters are given in Table 2. Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited under C.S.D. No. 55732 with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., W-7514 Eggenstein-Leopoldshafen 2, FRG.

TABLE 1

Crystallographic data for  $\text{Na}_4\text{Cu}_2\text{S}_3$ 

Pearson symbol	$tI144$
$a$ (Å)	9.468(1)
$c$ (Å)	36.64(2)
Space group	$I4_1/a$ (No. 88)
$Z$	16
$V$ (Å <sup>3</sup> )	3284(2)
$d$ (g cm <sup>-3</sup> )	2.55
Relative formula mass (RFM)	315.23
Absorption coefficient ( $\mu_{\text{Mo K}\alpha}$ ) (cm <sup>-1</sup> )	60.4
<i>Structure refinement</i>	
Unique reflections	1972
$F_o^2 > 3\sigma(F_o^2)$	1682
Refined variables	83
$R = \Sigma  F_o  -  F_c  / \Sigma  F_o $	0.021
$R_w = [\Sigma w( F_o  -  F_c )^2 / \Sigma w  F_o ^2]^{1/2}$	0.022
$w = [\sigma(I)^2 + (0.008F_o^2)^2]^{-1/2}$	
Residual electron density (e Å <sup>-3</sup> )	1.6

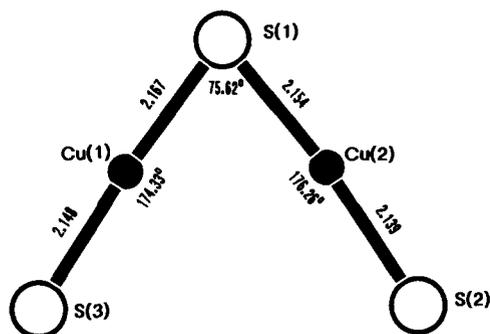
TABLE 2

Positional and equivalent isotropic thermal parameters for  $\text{Na}_4\text{Cu}_2\text{S}_3$ 

Atom	Wykoff position	$x$	$y$	$z$	$B_{\text{eq}}$ ( $\text{\AA}^2$ ) <sup>a</sup>
Na(1)	4a	0.000	0.250	0.125	1.41(3)
Na(2)	4b	0.500	0.750	0.125	1.72(3)
Na(3)	8e	0.000	0.250	0.03363(4)	1.84(3)
Na(4)	8e	0.000	0.750	0.11740(4)	1.57(3)
Na(5)	8e	0.500	0.250	0.03847(4)	1.90(3)
Na(6)	16f	0.2534(1)	0.9562(1)	0.03937(3)	1.60(2)
Na(7)	16f	0.2505(1)	0.4932(1)	0.11859(3)	1.49(2)
Cu(1)	16f	0.39582(3)	0.59947(4)	0.04544(1)	1.583(6)
Cu(2)	16f	0.11570(3)	0.59426(3)	0.04328(1)	1.501(6)
S(1)	16f	0.25733(7)	0.69667(6)	0.00546(2)	1.22(1)
S(2)	16f	0.98691(6)	0.48733(6)	0.08267(2)	1.11(1)
S(3)	16f	0.48369(6)	0.01114(6)	0.08622(2)	1.17(1)

<sup>a</sup> $B_{\text{eq}} = 1/3(B_{11} + B_{22} + B_{33})$ .

Estimated standard deviations are given in parentheses.

Fig. 1. The complex anion of  $\text{Na}_4\text{Cu}_2\text{S}_3$  (bond distances in  $\text{\AA}$ ).

#### 4. Discussion

The interatomic distances and bond angles for  $\text{Na}_4\text{Cu}_2\text{S}_3$  are given in Table 3. The crystal structure contains seven crystallographically independent sodium atoms, all of which occur in distorted tetrahedral sulphur co-ordinations ( $d_{\text{Na-S}}$  2.728–2.874  $\text{\AA}$ ), while the co-ordination for the two independent copper atoms is close to linear. As shown in Fig. 1, the copper atoms take part in the formation of unique V-shaped anionic groups  $[\text{S-Cu-S-Cu-S}]^{4-}$ . These groups have an almost  $C_{2v}$  symmetry with a mean Cu–S bond length of 2.152  $\text{\AA}$ , the Cu–S bonds to the terminal sulphur atoms being slightly shorter than those to the central S(1) atom. The bond angles on the copper

TABLE 3  
Interatomic distances (Å) and bond angles for Na<sub>4</sub>Cu<sub>2</sub>S<sub>3</sub>

Bond	Distance (Å)	Angle (deg)
<i>Co-ordination of the Na<sup>+</sup> cations</i>		
Na(1)–S(2)	2.728(1) (4×)	
Na(1)–Na(3)	3.341(1) (2×)	
Na(1)–Na(7)	3.308(1) (2×)	
S(2)–Na(1)–S(2)		108.78(2) (4×)
S(2)–Na(1)–S(2)		110.86(2) (2×)
Na(2)–S(3)	2.8504(6) (4×)	
Na(2)–Cu(1)	3.3846(3) (4×)	
Na(2)–Na(7)	3.392(1) (4×)	
S(3)–Na(2)–S(3)		104.33(2) (4×)
S(3)–Na(2)–S(3)		120.33(2) (2×)
Na(3)–S(1)	2.865(1) (2×)	
Na(3)–S(2)	2.874(1) (2×)	
Na(3)–Cu(2)	3.357(1) (2×)	
Na(3)–Cu(2)	3.4501(4) (2×)	
Na(3)–Na(6)	3.673(1) (2×)	
S(1)–Na(3)–S(2)		97.90(2) (2×)
S(2)–Na(3)–S(2)		102.79(5)
S(1)–Na(3)–S(2)		119.01(2) (2×)
S(1)–Na(3)–S(1)		120.16(5)
Na(4)–S(2)	2.791(1) (2×)	
Na(4)–S(3)	2.828(1) (2×)	
Na(4)–Cu(2)	3.272(1) (2×)	
Na(4)–Na(5)	3.442(2)	
Na(4)–Na(7)	3.340(1) (2×)	
Na(4)–Na(7)	3.332(1) (2×)	
S(2)–Na(4)–S(3)		105.06(2) (2×)
S(3)–Na(4)–S(3)		106.28(5)
S(2)–Na(4)–S(3)		106.62(2) (2×)
S(2)–Na(4)–S(2)		125.87(6)
Na(5)–S(1)	2.845(1) (2×)	
Na(5)–S(3)	2.858(1) (2×)	
Na(5)–Cu(1)	3.4555(3) (2×)	
Na(5)–Cu(1)	3.523(1) (2×)	
Na(5)–Na(6)	3.625(1) (2×)	
S(1)–Na(5)–S(3)		99.30(2) (2×)
S(3)–Na(5)–S(3)		104.69(5)
S(1)–Na(5)–S(1)		111.25(5)
S(1)–Na(5)–S(3)		121.90(2) (2×)
Na(6)–S(1)	2.749(1)	
Na(6)–S(1)	2.802(1)	
Na(6)–S(3)	2.817(1)	
Na(6)–S(2)	2.820(1)	
Na(6)–Cu(1)	3.363(1)	
Na(6)–Cu(2)	3.524(1)	
Na(6)–Cu(2)	3.540(1)	
Na(6)–Cu(1)	3.637(1)	
Na(6)–Cu(1)	3.642(1)	

(continued)

TABLE 3 (continued)

Bond	Distance (Å)	Angle (deg)
Na(6)—Cu(2)	3.663(1)	
Na(6)—Na(7)	3.392(1)	
S(1)—Na(6)—S(2)		100.70(4)
S(1)—Na(6)—S(3)		101.31(4)
S(2)—Na(6)—S(3)		104.23(4)
S(1)—Na(6)—S(3)		115.36(4)
S(1)—Na(6)—S(2)		115.66(4)
S(1)—Na(6)—S(1)		117.35(4)
Na(7)—S(3)	2.778(1)	
Na(7)—S(3)	2.812(1)	
Na(7)—S(2)	2.815(1)	
Na(7)—S(2)	2.816(1)	
Na(7)—Cu(1)	3.170(1)	
Na(7)—Cu(2)	3.181(1)	
S(2)—Na(7)—S(2)		103.94(4)
S(2)—Na(7)—S(3)		104.51(4)
S(2)—Na(7)—S(3)		104.81(4)
S(3)—Na(7)—S(3)		107.33(4)
S(2)—Na(7)—S(3)		107.35(4)
S(2)—Na(7)—S(3)		126.93(4)
<i>Geometry of the [Cu<sub>2</sub>S<sub>3</sub>]<sup>4-</sup> anion</i>		
Cu(1)—S(3)	2.1476(7)	
Cu(1)—S(1)	2.1666(7)	
Cu(1)—Cu(2)	2.6488(4)	
Cu(1)—Cu(1)	3.4600(5) <sup>a</sup>	
S(1)—Cu(1)—S(3)		174.33(3)
Cu(2)—S(2)	2.1394(7)	
Cu(2)—S(1)	2.1542(7)	
Cu(2)—Cu(2)	3.6669(5) <sup>a</sup>	
S(1)—Cu(2)—S(2)		176.26(3)
Cu(1)—S(1)—Cu(2)		75.62(2)

<sup>a</sup>Closest Cu—Cu distances between neighbouring groups.  
Estimated standard deviations are given in parentheses.

atoms are close to 175°; that on the S(1) atom is 75.62°. These values compare well with those found in the infinite anionic zig-zag chains of KCuS [12] ( $d_{\text{Cu-S}} = 2.145 \text{ Å}$ ,  $\angle \text{S-Cu-S} = 179.0^\circ$ ,  $\angle \text{Cu-S-Cu} = 76.6^\circ$ ). Comparison with CsCu<sub>3</sub>S<sub>2</sub> [13], the only other alkali thiocuprate with linearly co-ordinated Cu(I), reveals a very weak dependence of the Cu—S bond length on the coordination number of the chalcogen. The hexagonal anionic sheets contain  $\mu_3$ -coordinating sulphur; a slightly larger Cu—S bond length of 2.166 Å is observed.

Although Na<sub>4</sub>Cu<sub>2</sub>S<sub>3</sub> crystallizes with a surprisingly large unit cell, its crystal structure may still be related to quite simple packing principles. Essentially, as in the binary sulphide Na<sub>2</sub>S (anti CaF<sub>2</sub> type), the packing is characterized by a cubic close-packed arrangement of the chalcogen atoms with the sodium ions in (distorted) tetrahedral voids. As in the related structure

of  $\text{Na}_3\text{AgS}_2$  [14] the coinage metal atoms do not, however, simply substitute for the sodium atoms in the crystal structure, but are shifted from the centres of the tetrahedra towards the edges, thus attaining an almost linear sulphur co-ordination. This complexity arises from the fact that the identity period  $c$  (as shown in Fig. 2) comprises 12 cation layers in an alternating sequence. After a pair of mixed layers, each built up by the copper atoms and the sodium atoms Na(2), Na(5) and Na(6), follows a pure sodium layer built up by the remaining sodium atoms at  $z \approx (2n + 1)/8$ . The neighbouring mixed layers are crystallographically related to each other by the mirror glide planes at  $z = 0, 0.25, 0.5$  and  $0.75$ .

A single mixed layer and its adjacent sulphur atoms are shown in Fig. 3. The edge-sharing  $\text{NaS}_4$  tetrahedra are arranged in zig-zag rows, separated from each other by corresponding rows of vacant tetrahedra. The copper

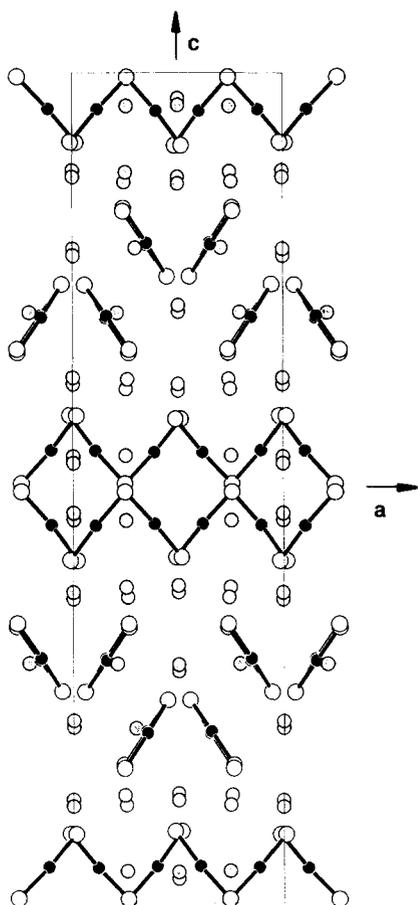


Fig. 2. Projection of the unit cell of  $\text{Na}_4\text{Cu}_2\text{S}_3$  along [100]. Shaded circles, sodium; full circles, copper; open circles, sulphur. Cu-S bonds are indicated by heavy lines.

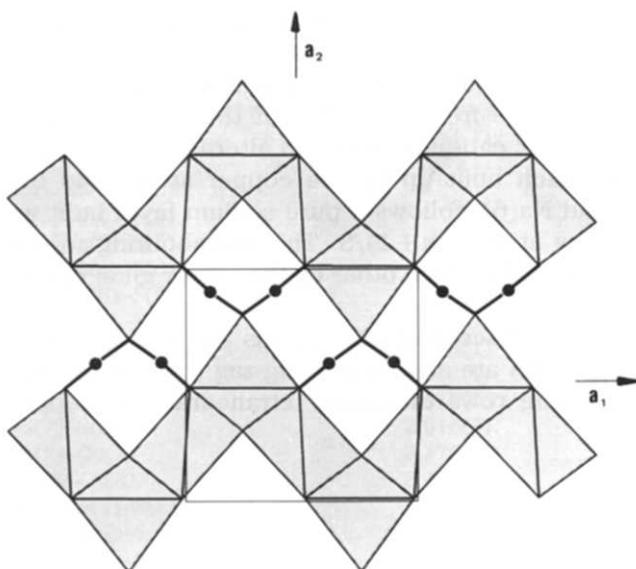


Fig. 3. The mixed tetrahedral layer as seen in projection along [001]. Sodium atoms occupy the centres of the dotted tetrahedra. Copper atoms (full circles) centre two adjoining edges of every second vacant sulphur tetrahedron. Cu-S bonds are indicated by heavy lines.

atoms centre the two adjoining edges of every second vacant sulphur tetrahedron, thus forming the V-shaped thiocuprate ions.

The complex anion in  $\text{Na}_4\text{Cu}_2\text{S}_3$  represents the first example of an oligomeric group which belongs to a hypothetical series  $[\text{M}_n\text{X}_{n+1}]^{(n+2)-}$  ( $\text{M}$  = coinage metal,  $\text{X}$  = chalcogen) of chain-type anions formed by linearly co-ordinated metal atoms and  $\mu_2$ -bridging chalcogen atoms. For  $n = \infty$ , this series yields the infinite zig-zag chains,  $\infty^1\text{-}[\text{MX}]^-$ , found in  $\text{KCuS}$  [12] and in  $\text{KAuS}$  or  $\text{KAuSe}$  [15], while for  $n = 1$ , the monomeric dumbbell-shaped anions of  $\text{Na}_3\text{AgS}_2$  [14] or  $\text{Na}_3\text{AuS}_2$  [16] are formed. Since the cation-rich sections of the systems  $\text{A-M-X}$  ( $\text{A}$  = alkali metal) have not been thoroughly investigated, other oligomeric members of this series might well exist. Since among the coinage metal  $d^{10}$  ions  $\text{Au(I)}$  has the highest preference for linear co-ordination, investigations in the corresponding gold systems might prove most promising for searching for such oligomeric chain-type anions. So far,  $\text{Na}_7\text{Au}_5\text{S}_6$  [17] is the only other intermediate compound besides  $\text{Na}_4\text{Cu}_2\text{S}_3$  which formally belongs to this series. However, it does not contain finite pentameric  $[\text{Au}_5\text{S}_6]^{7-}$  chains, but instead its anionic partial structure is characterized by the coexistence of infinite chains  $\infty^1\text{-}[\text{AuS}]^-$  and monomeric  $[\text{AuS}_2]^{3-}$  groups.

Discrete complex anions with linearly co-ordinated metal atoms could, in principle, also be obtained by the nucleophilic attack on the infinite chain

of red HgS [18] by alkali sulphides. In this way, almost linear  $[\text{S-Hg-S}]^{2-}$  anions are obtained in the crystal structures of  $\text{Na}_2\text{HgS}_2$  and  $\text{K}_2\text{HgS}_2$  [19]. However, in higher thiomercurates the linear co-ordination of the mercury atoms is only retained in part, while the remaining mercury atoms acquire higher sulphur co-ordinations. Thus, the structures of  $\text{K}_2\text{Hg}_3\text{S}_4$  [20],  $\text{Na}_2\text{Hg}_3\text{S}_4$  [21] and  $\text{K}_2\text{Hg}_6\text{S}_7$  [20] are characterized by infinite complex anions.

### Acknowledgments

The authors are grateful to the Austrian Federal Ministry for Science and Research and to the Linzer Hochschulfonds for the support of this study.

### References

- 1 Chr. Burschka, *Z. Naturforsch. Teil B*, **34** (1979) 396.
- 2 G. Savelsberg and H. Schäfer, *Mater. Res. Bull.*, **16** (1981) 1291.
- 3 W. Bronger and Chr. Burschka, *Z. Anorg. Allg. Chem.*, **425** (1976) 109.
- 4 H. Effenberger and F. Pertlik, *Monatsh. Chem.*, **116** (1985) 921.
- 5 W. Rüdorff, H. G. Schwarz and M. Walter, *Z. Anorg. Allg. Chem.*, **269** (1952) 141.
- 6 N. I. Kopylov, S. S. Novoselov, L. A. Yuzvak and A. A. Kashaev, *Zh. Neorg. Khim.*, **9** (1964) 1403.
- 7 K. Friedrich, *Metallurgie*, **11** (1914) 160.
- 8 G. Bodländer and K. S. Idaszewski, *Z. Elektrochem.*, **11** (1905) 161.
- 9 P. Main, J. S. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, *MULTAN 82, a System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, University of York, 1982.
- 10 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.
- 11 *MolEN, An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, 1990.
- 12 G. Savelsberg and H. Schäfer, *Z. Naturforsch. Teil B*, **32** (1978) 711.
- 13 Chr. Burschka, *Z. Anorg. Allg. Chem.*, **463** (1980) 65.
- 14 K. O. Klepp and W. Bronger, *J. Less-Common Met.*, **106** (1985) 95.
- 15 K. O. Klepp and W. Bronger, *J. Less-Common Met.*, **132** (1987) 173.
- 16 K. O. Klepp and W. Bronger, *J. Less-Common Met.*, **127** (1987) 65.
- 17 K. O. Klepp and G. Brunnbauer, *J. Alloys Comp.*, **183** (1992) 252.
- 18 P. Auvray and F. Genet, *Bull. Soc. Fr. Minér. Crist.*, **96** (1973) 218.
- 19 K. O. Klepp and K. Prager, *Z. Naturforsch. Teil B*, in the press.
- 20 M. G. Kanatzidis and Y. Park, *Chem. Mater.*, **2** (1990) 99.
- 21 K. O. Klepp, *J. Alloys Comp.*, **182** (1992) 281.