$Nb_4Te_{17}I_4$, a New Pseudo One-Dimensional Solid-State Polytelluride

Wolfgang Tremel

Institut für Anorganische Chemie und Analytische Chemie, Universität Mainz,
Becherweg 24, D-55128 Mainz, FRG

The new ternary compound $Nb_4Te_{17}I_4$ has been prepared and structurally characterized. It crystallizes in the monoclinic system, space group $C2/c$ with unit-cell parameters $a = 16.199(4)$, $b = 8.128(2)$, $c = 27.355(6)$ Å, $\beta = 110.84(2)°$, $Z = 4$. The structure consists of infinite one-dimensional niobium/tellurium chains running parallel to the crystallo-graphic c direction. The chains are separated by iodine atoms. Short and long metal–metal distances alternate in the sequence of three consecutive short bonds ($[\bar{d} \approx 3.1–3.2$ Å) and one long ($d = 4.268$ Å) metal–metal separation. Each Nb atom is eight-coordinate. The composition of the chain is $\frac{1}{\infty}[(Nb^{5+})_2(Nb^{4+})_2(Te_2^{2-})_4(Te_3^{2-})_3(I^-)_4]$.

In the past ten years inorganic conductors with one-dimensional character, such as $NbSe_3$[1], $K_{0.3}MoO_3$[2], or $(TaSe_4)_2I$[3] have attracted much attention in solid-state chemistry and physics. The prime reason for this was the discovery of marked non-linear and frequency-dependent electrical transport phenomena in the charge-density wave state associated with a Peierls distortion[4]. These striking properties have stimulated numerous chemical attempts to synthesize new or to modify known compounds with the aim at getting new materials with similar properties.

In the course of these studies much synthetic effort has been devoted to transition metal chalcogenides, especially sulfides and selenides. The rationale behind this selection is that the high ionicity of oxides prevents the formation of one-dimensional solids. Chalcogen-rich sulfides and selenides seemed to be the most promising class of compounds to find 1D (and 2D) materials, whereas tellurides, which are generally considered to be highly covalent and often quasi-metallic compounds, received almost no attention.

From a chemical point of view this is surprising. Solid-state tellurides such as $ZrTe_5$[5], MTe_4 (M = Nb, Ta)[6], Ta_2Te_3[7], Ta_4SiTe_4[8], or $TaNi_2Te_2$[9] show a stunning structural diversity. These compounds have no analogs among the sulfides and selenides, suggesting that the transition metal tellurides should be very different from the other chalcogenides. The assumptions find support by several molecular examples. Species such as $KAu_9Te_7^{4-}$[10], $NbTe_{10}^{3-}$[11], or $As_{10}Te_3^{2-}$[12] display a large structural variety and have no counterpart in sulfur or selenium chemistry.

As with any chemical assemblage, the physical properties of the transition metal chalcogenides arise from the peculiar association of their crystal and electronic structures. New and perhaps unusual properties might be found by studying materials with new structures. Therefore, we initiated a program to investigate the chemistry, structure and properties of new ternary early transition metal tellurides. One possible synthetic approach starts from the binary metal tellurides $NbTe_2$ and $NbTe_4$, which can be formally reduced (e.g. with alkali or late transition metals) or oxidized (e.g. with halogens). Oxidation reactions lead to the synthesis of several new niobium chalcogenide iodides. In this paper we

describe the synthesis and structure of $Nb_4Te_{17}I_4$, a new one-dimensional polytelluride.

Results and Discussion

Figure 1 shows a [001] projection of the structure. The presence of infinite chains running parallel to the c direction is immediately apparent. The (centered) unit cell contains two identical chains.
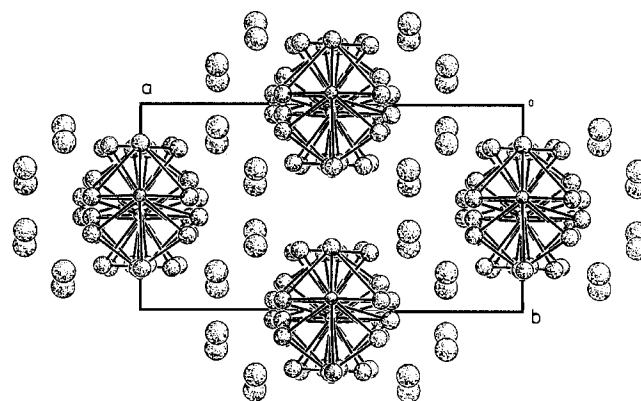

Figure 1. [001] projection of the $Nb_4Te_{17}I_4$ structure; large, isolated circles: I; small circles: Nb; medium circles: Te

The parallel chains are well separated from each other by halogen atoms. The shortest Te–Te *interchain* contacts are more than 4.0 Å, the center-to-center separation being ca. 9.06 Å. This provides a pseudo one-dimensional character to this compound. The relative orientation of the chains within the unit cell as well as the linear character of the chains, which are completely sheathed by iodine atoms, is also apparent from Figure 1. The iodine atoms separating the chains exhibit asymmetric coordination: atoms I(1) and I(2) are coordinated by six Te atoms. The I···Te distances are in the range between 3.170(2) and 3.898(2) Å. Figure 2 shows two views of a single one-dimensional $\frac{1}{\infty}[Nb_4Te_{17}]$ chain (together with the iodine atoms closest to this chain).

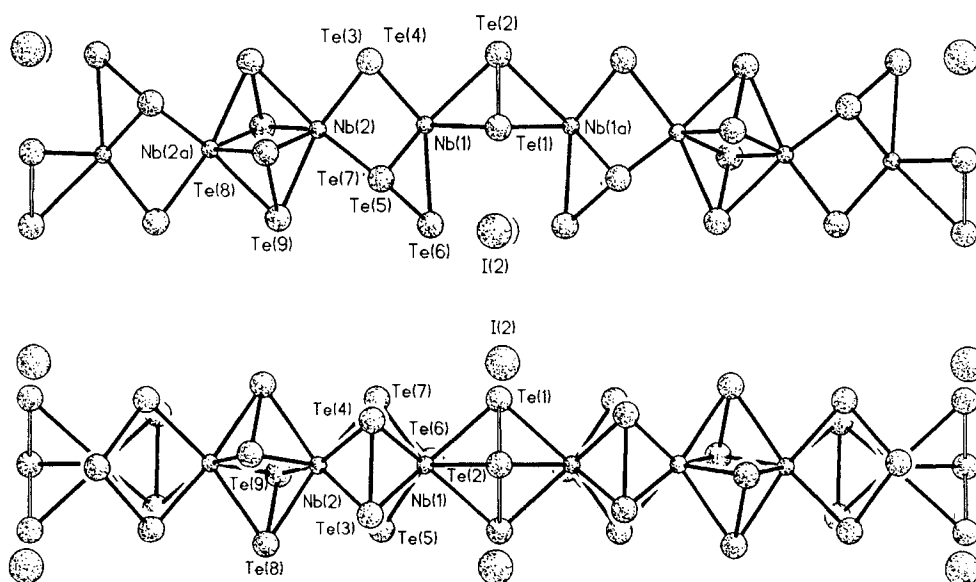Figure 2. Two views of the $\frac{1}{\infty}[Nb_4(Te_2^{2-})_4(Te_3^{2-})_3]$ chain (with atom labeling) including the nearest iodine atoms

Along the chain eight metal atoms are found within one translational period along c. Short and long metal–metal distances alternate in such a way that after three consecutive short Nb–Nb distances [$d_{Nb(1)-Nb(2)}$ = 3.133(2) Å; $d_{Nb(2)-Nb(2A)}$ = 3.212(2) Å, $d_{Nb(1A)-Nb(2A)}$ = 3.133(2) Å] one long Nb–Nb [$d_{Nb(1)-Nb(1A)}$ = 4.268(2) Å] distance occurs. From another point of view one might say that each chain is built up from linear tetranuclear Nb$_4$ clusters separated by a bridge [corresponding to the long Nb(1)−Nb(1a) distance]. Each Nb$_4$ segment contains a crystallographically imposed inversion center, two consecutive segments are connected by a c-glide plane. Thus, each chain contains two crystallographically distinct Nb atoms.

Looking at the Nb environment, we find different coordination polyhedra. Nb(2) is eight-coordinate and has a rectangular antiprismatic environment. This type of coordination is found in several related linear-chain compounds such as $(NbSe_4)_3I^{[13]}$ or $(NbSe_4)_{10/3}I^{[14]}$. Two adjacent rectanglular Te$_4$ planes always adopt a staggered orientation. This minimizes repulsive interactions between the Te atoms of neighboring Te$_2$ groups.

Nb(1), the second symmetry-independent metal atom, has a very irregular Te coordination. On one side there is a distorted Te$_4$ rectangle [Te(3), Te(4), Te(5), Te(7)] which separates it from Nb(2). On the other side one finds a Te$_3$ fragment bridging Nb(1) and Nb(1A). In addition, there is one Te atom, Te(6), which is part of a Te$_3$ group [Te(5)−Te(6)−Te(7)] and is bound only to one metal atom, Nb(1). Thus, the Nb(1) coordination might be described as capped trigonal-bipyramidal where a single Te atom of the trigonal bipyramid is replaced by a Te$_2$ group [Te(3)−Te(4)]. A similar type of Nb coordination has been found in $Nb_6Se_{20}Br_6^{[15]}$.

Let us focus next on the ligands and their modes of coordination. Each chain contains two different ligands in three modes of coordination: (i) $\mu-\eta^2:\eta^2$-Te$_2$ groups are bridging Nb(2) and Nb(2A). The Te−Te distance of these Te$_2$ groups [$d_{Te(8)-Te(9)}$ = 2.792(1) Å] is typical of a Te−Te single bond.

This bridging mode is known from many linear chain compounds such as $NbTe_4I^{[16]}$, $(MSe_4)_nI$ (M = Nb, Ta; n = 2, 3, 10/3; with bridging $\mu-\eta^2:\eta^2$-Se$_2$ groups)$^{[13,14]}$ or VS$_4$ (with bridging $\mu-\eta^2:\eta^2$-S$_2$ groups)$^{[17]}$, and molecular compounds such as $V_2(S_2)_2(S_2CN iBu_2)_4^{[18]}$. (ii) $\mu-\eta^2:\eta^3$-Te$_3$ groups are bridging Nb(1) and Nb(1A). The Te−Te distances of this Te$_3$ ligand [$d_{Te(1)-Te(2)}$ = 2.857(1) Å] are also well within the single-bond range, although they are significantly longer than all other Te−Te distances of the molecule. This bond lengthening might arise from weak Te−I interactions. The Te(1)−I(2) distance is 3.170(2) Å. This value can be compared to a Te⋯I van der Waals distance of 4.25 Å and a value of 2.69 Å for the sum of the covalent radii of tellurium and iodine. Therefore, it seems reasonable to assume that lengthening of the Te(1)−Te(2) bond may be caused (at least in part) by a hypervalency of Te(1). (iii) Finally, the chains contain Te$_3$ groups [Te(5)−Te(6)−Te(7)] whose terminal atoms Te(5) and Te(7) are bridging two metal atoms. The central atom, Te(6), however, is bound only to one niobium atom. Thus, the bridging mode might be described as $\mu-\eta^2:\eta^1:\mu-\eta^2$. The central tellurium atoms are responsible for lengthening of the Nb(1)−Nb(1A) distance to 4.268 Å. A shorter Nb−Nb distance would lead to too short van der Waals contacts between adjacent Te(6) atoms. One geometrical consequence of this distortion is the formation of cavities along the chain. In the $Nb_4Te_{17}I_4$ structure these cavities are "filled" by the I(2) atoms, the distances I(2)−Te(1) and I(2)−Te(6) being 3.169(1) Å and 3.588(1) Å. The Te−I interaction within the chains is much stronger than the Te−I interaction between neighboring chains. This can be seen from the interchain Te−I distances [e.g. $d_{Te(8B)-I(1)}$ = 3.851(2) Å; $d_{Te(4B)-I(2)}$ = 3.533(2) Å]. Thus, $Nb_4Te_{17}I_4$ can really be viewed as a 1D compound built up in a first approximation by the alignment of Nb_4Te_{17} chains separated by iodine atoms.

In addition, it might be interesting to compare the shortest Te−I distances with Te−Br, Se−Br, and Se−I distances

in related compounds. In $(NbSe_4)_{10/3}I^{[14]}$, for example, the distance between I atoms separating the $NbSe_4$ chains and Se atoms of the chains is 3.272 Å. The shortest corresponding Se—Br distance in $Nb_6Se_{20}Br_6$ is 3.03 Å[15], whereas the Te—Br distance in $MoTe_4Br^{[19]}$ is also 3.03 Å. An estimate of the chalcogen—halogen bond orders using Pauling's relation[20] $d(n) = d(1) - 0.6\log n$ gives calculated bond orders of 0.07, 0.06, 0.16, and 0.13. These values indicate that Q—X interaction increases with increasing electronegativity difference between the chalcogen atoms (Q) of the chain and the halogen atoms separating the chains (X) and decreasing size of the halogen (i.e. increasing polarization of the Q—X bond). A series of $(NbQ_4)_nX$ compounds has been reported for the selenium/iodine system[13,14] (where the electronegativity difference Q/X is smallest), but only a single compound is known from the Te/Br system. We are not aware of any structurally related material from the Q/Cl system (where the Q—X interaction would be largest).

A formal description of the electronic structure of the title compound would be $(Nb^{5+})_2(Nb^{4+})_2(Te_2^{2-})_4(Te_3^{2-})_3$-$(I^-)_4$ where this formulation does of course not imply a fully ionic character. According to this description the "conduction band" of this chain compound is half filled. The Nb—Nb bond distances, however, indicate that both 4d electrons are not delocalized along the chain but rather trapped within the linear "Nb₄ clusters", where they occupy the lowest Nb—Nb bonding MOs. Therefore, semiconducting properties should be expected for Nb₄Te₁₇I₄.

The fact that our attempts to perform a direct replacement of the Se atoms in the $(NbSe_4)_nI$ compounds by tellurium atoms has not been successful so far gives some clues concerning the stability of the corresponding structure types. It is well-known that the stability of these one-dimensional materials is mainly determined by (i) the extent of repulsion between the chains and (ii) the extent of bonding through the van der Waals gap. High ionicity (e.g. in oxides) counteracts the formation of low-dimensional structures. On the other hand, strong interchain interaction causes the low-dimensional character to decrease.

One factor which is important for the stability of low-dimensional chalcogen halides (and especially for the chalcogen iodides) is the tendency of the metal/chalcogen chain to resist oxidation. In general, tellurides are oxidized easier than selenides and sulfides. For the niobium (or tantalum) tellurides there seem to be two options to circumvent the formation of partially oxidized systems: (i) formal oxidation of the metal leads to a d⁰ electron count as found in NbTe₄I and TaTe₄I[19]; (ii) oxidation of the chalogen leads to the formation of polytellurides as found in Nb₄Te₁₇I₄. Selenides are oxidized less easily. Therefore, partially oxidized one-dimensional compounds with a formal $d^{\frac{n-1}{n}}$ electron count such as $(TaSe_4)_nI$ and $(NbSe_4)_nI$ ($n = 2$ for Ta; 3, 10/3 for Nb) are found[2,16,17]. The lowest d bands for these compounds contain $(n - 1)/n$ electrons, i.e. these materials should be metallic in the absence of a Peierls distortion. For the corresponding sulfides, one might speculate that it would be not possible to perform even partial oxidation to

$(NbS_4)_nI$- or $(TaS_4)_nI$-type materials. One might be trapped at compositions NbS_4 or TaS_4, respectively. These compounds, however, are probably too ionic to exist as one-dimensional species. Therefore (among the chalcogenide halides), the selenides seem to be the most promising group of compounds for the design of chalcogen-rich conducting one-dimensional materials.

Experimental

Synthesis: Starting materials were niobium powder (Starck, 99.99% purity), tellurium powder (Merck, 99.9% purity), and doubly sublimed iodine. Crystals of Nb₄Te₁₇I₄ were obtained initially from preparations aimed at obtaining $(NbTe_4)_nI$ analogous to the $(NbSe_4)_nI$ ($n = 2, 3, 10/3$) phases. Mixtures of the elements in a ratio of Nb:Te:I = 2:9:2 were heated in vacuo in sealed silica tubes at 470°C for three weeks. Guinier photographs indicated the presence of a small amount of elemental tellurium and an unknown phase. A microanalysis of this phase by energy-dispersive X-ray fluorescence indicated the presence of Nb, Te and I in the approximate ratio of 1:4:1. Single-phase material could be obtained by heating niobium, tellurium, and iodine in a ratio of 4:17:4 in a temperature gradient (490−540°C) for two weeks followed by radiative cooling to room temperature. A slight excess of tellurium was helpful to suppress the formation of the adjacent phase NbTe₄I. Nb₄Te₁₇I₄ crystals are black and show metallic luster. They are air-stable for several days. Although the optimum temperature range for obtaining Nb₄Te₁₇I₄ is 490−540°C, it can also be prepared by allowing the elements to react at higher temperatures (up to 640°). Nb₄Te₁₇I₄ was synthesized from the elements in quartz ampoules. The ampoules (length ca. 12 cm, i.d. ca. 12 mm) were flame-dried in vacuo and subsequently filled with niobium powder (0.186 g, 2.000 mmol), tellurium powder (1.085 g, 8.500 mmol) and iodine (0.254 g, 2.000 mmol). The ampoules were sealed in vacuo and heated slowly to 480°C. After 10 d, the furnace was switched off and cooled radiatively. Black needles with a metallic luster had formed; yield 0.928 g (61%). − Analysis (EDAX): Nb:Te:I = 1.02:4.26:1.09.

Structure Determination. − a) *Collection and Reduction of X-ray Data:* Nb₄Te₁₇I₄ crystals have a block-like habit. A preliminary X-ray investigation by standard camera methods revealed a Laue symmetry 2/m. The systematic extinctions (hkl, h + k = 2n; h0l, l = 2n) are compatible with the space groups Cc or C2/c, of which only the centrosymmetric group C2/c was found to be correct during the structure determination. A crystal measuring approximately 0.12 × 0.12 × 0.15 mm was mounted at the top of a glass capillary

Table 1. Crystallographic data and data-collection details for Nb₄Te₁₇I₄

Empirical formula: Nb₄Te₁₇I₄; mol. mass: 3048.44; crystal size: 0.12 × 0.12 × 0.15 mm; space group: C2/c; Z = 4; temperature: 298 K; $a = 16.199(4)$, $b = 8.128(2)$, $c = 27.355(6)$ Å; $\beta = 110.84(2)°$; $V = 3366(2)$ Å³; $\rho_{calcd.} = 6.016$ g/cm³; $\mu = 19.40$ mm⁻¹, radiation: Mo K_α, $\lambda = 0.71073$ Å; $2\Theta_{max.} = 60°$; total no. of unique reflections: 5255; $R = 0.046$; $R_w = 0.046$ [$w = 1/\sigma^2(F_o)$]; residual electron density: −2.4 (min.), +2.5 (max.) e⁻/Å

Table 2. Positional parameters and equivalent isotropic displacement coefficients [Å²][a] for Nb₄Te₁₇I₄

atom	x/a	y/b	z/c	U_{eq}
Nb(1)	-0.00086(5)	0.55660(10)	0.67186(3)	0.0102(2)
Nb(2)	-0.00157(5)	0.53678(10)	0.55734(3)	0.0108(2)
Te(1)	-0.12589(4)	0.54902(9)	0.72360(2)	0.0173(2)
Te(2)	0	0.81091(12)	3/4	0.0247(3)
Te(3)	-0.09672(4)	0.78302(8)	0.59254(2)	0.0176(2)
Te(4)	0.08406(4)	0.79624(8)	0.63303(2)	0.0179(2)
Te(5)	-0.12369(4)	0.36364(8)	0.59931(2)	0.0166(2)
Te(6)	0.00666(5)	0.20146(8)	0.67947(3)	0.0193(2)
Te(7)	0.12517(4)	0.37325(9)	0.64702(2)	0.0176(2)
Te(8)	-0.15267(4)	0.45383(9)	0.46914(2)	0.0185(2)
Te(9)	-0.01893(5)	0.22182(8)	0.51089(2)	0.0185(2)
I(1)	-0.30095(5)	0.60834(10)	0.55572(3)	0.0286(2)
I(2)	-0.19562(5)	0.18156(14)	0.70491(3)	0.0422(3)

[a] The U_{eq} values [Å²] are defined as 1/3 of the trace of the orthogonalized U_{ij} tensor: $U_{eq} = 1/3 \sum_{ij} U_{ij}a^*_i a^*_j a_i a_j$

Table 3. Interatomic distances [Å][a] for Nb₄Te₁₇I₄ (standard deviations)

	Distances			Distances	
Nb(1)	- Nb(2)	3.133(2)	Te(1)	- Te(2)	2.857(1)
Nb(2)	- Nb(2A)	3.212(2)	Te(3)	- Te(4)	2.740(1)
Nb(1)	- Nb(1A)	4.268(2)	Te(5)	- Te(6)	2.777(1)
			Te(6)	- Te(7)	2.763(1)
Nb(1)	- Te(1)	2.854(2)	Te(8)	- Te(9)	2.792(1)
Nb(1)	- Te(1A)	2.867(1)			
Nb(1)	- Te(2)	2.970(2)	I(1)	... Te(3)	3.407(2)
Nb(1)	- Te(3)	2.848(1)	I(1)	... Te(5)	3.345(2)
Nb(1)	- Te(4)	2.803(2)	I(1)	... Te(3B)	3.898(2)
Nb(1)	- Te(5)	2.747(1)	I(1)	... Te(7A)	3.799(2)
Nb(1)	- Te(6)	2.893(1)	I(1)	... Te(8B)	3.651(2)
Nb(1)	- Te(7)	2.800(2)	I(1)	... Te(9A)	3.426(2)
Nb(2)	- Te(3)	2.892(2)			
Nb(2)	- Te(4)	2.935(1)	I(2)	... Te(1)	3.170(1)
Nb(2)	- Te(5)	2.971(2)	I(2)	... Te(5)	3.780(2)
Nb(2)	- Te(7)	2.901(1)	I(2)	... Te(6)	3.588(2)
Nb(2)	- Te(8)	2.840(1)	I(2)	... Te(4B)	3.533(2)
Nb(2)	- Te(8A)	2.839(2)	I(2)	... Te(6B)	3.537(2)
Nb(2)	- Te(9)	2.827(1)	I(2)	... Te(7B)	3.734(2)
Nb(2)	- Te(9A)	2.808(2)			

[a] Symmetry codes: $1 - x, -y, -z$ (atoms labeled with A); $2 - x, -y, -z$ (atoms labeled with B); x, y, z (all other atoms).

with epoxy glue. X-ray diffraction data were recorded with an automated Siemens R3m/V four-circle diffractometer with graphite-monochromated Mo-K_α radiation. The unit-cell dimensions and their standard deviations were determined from a least-squares fit of the setting angles of 24 reflections in the range $20° \leq 2\Theta \leq 50°$. Data were collected in the ω-scan mode. The intensities of two standard reflections measured every 98 scans revealed no significant changes during the data collection. The intensity profiles of all reflections indicated stable crystal settings. – All calculations were done by using the SHELXTL PLUS program package. An empirical absorption correction was applied to the data by using the XEMP routines of the SHELXTL PLUS program package[20]. Lorentz and polarization effects were taken into account as usual. Further details relevant to the data collection and structure refinement are given in Table 1 and in ref.[22].

b) *Solution and Refinement of the Structure:* The structure was solved by direct methods (SHELXS), which revealed the initial positions of several heavy atoms (Te/I). The remaining heavy atoms were located from difference Fourier maps computed after least-squares cycles. Conventional atomic scattering factors were used[23a] and corrected for anomalous dispersion[23b]. An isotropic secondary extinction parameter was also refined. Calculations, performed at an intermediate stage in which the relative positional occupancies were refined, did not indicate any deviation from the composition Nb₄Te₁₇I₄. The final refinements resulted in the conventional residual values $R = 0.046$ and $Rw = 0.046$. Details concerning the structure solution and refinements are compiled in Table 1. The final atomic parameters and interatomic distances and angles are listed in Tabes 2 and 3. Further details of the crystal-structure investigations are available on request from the Fachinformationszentrum mbH, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-57498, the name of the author, and the journal citation.

[1] A. Meerschaut, J. Rouxel, *J. Less-Common Met.* **1975**, *39*, 197.
[2] Two recent reviews with numerous references are: M. Greenblatt, *Chem. Rev.* **1988**, *88*, 31; E. Canadell, M.-H. Whangbo, *Chem. Rev.* **1991**, *91*, 965.
[3] [3a] P. Gressier, A. Meerschaut, L. Guémas, J. Rouxel, P. Monceau, *J. Solid State Chem.* **1984**, *51*, 141. – [3b] P. Gressier, L. Guémas, A. Meerschaut, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2877. – [3c] P. Gressier, M.-H. Whangbo, A. Meerschaut, J. Rouxel, *Inorg. Chem.* **1984**, *23*, 1221.
[4] [4a] R. E. Peierls, *Quantum Theory of Solids*, Oxford University Press, London, **1955**, p. 108. – [4b] M.-H. Whangbo, *Acc. Chem. Res.* **1983**, *16*, 95.
[5] S. Furuseth, L. Brattås, A. Kjekshus, *Acta Chem. Scand. (1947–1973)* **1973**, *27*, 2367.
[6] K. Selte, A. Kjekshus, *Acta Chem. Scand. (1947–1973)* **1964**, *18*, 690; E. Bjerkelund, A. Kjekshus, *J. Less-Common Met.* **1964**, *7*, 231.
[7] [7a] M. Conrad, B. Harbrecht, *J. Alloys and Comp.* **1992**, *187*, 181. – [7b] H. Kleinke, Diploma Thesis, University of Münster, **1991**.
[8] M. E. Badding, F. J. DiSalvo, *Inorg. Chem.* **1990**, *29*, 3952.
[9] W. Tremel, *Angew. Chem.* **1992**, *104*, 230; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 217.
[10] R. C. Haushalter, *Angew. Chem.* **1985**, *97*, 412; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 432.
[11] W. A. Flomer, J. W. Kolis, *J. Am. Chem. Soc.* **1988**, *110*, 3682.
[12] R. C. Haushalter, *J. Chem. Soc., Chem. Commun.* **1987**, 196.
[13] A. Meerschaut, P. Palvadeau, J. Rouxel, *J. Solid State Chem.* **1977**, *20*, 21.
[14] A. Meerschaut, P. Gressier, L. Guemas, J. Rouxel, P. Monceau, *J. Solid State Chem.* **1984**, *51*, 307.
[15] A. Meerschaut, P. Grenouilleau, J. Rouxel, *J. Solid State Chem.* **1986**, *61*, 90.
[16] W. Tremel, *Chem. Ber.* **1992**, *125*, 2165.
[17] R. Allman, I. Baumann, A. Kutoglu, H. Rosch, E. Hellner, *Naturwissenschaften* **1964**, *263*, 1964.
[18] T. R. Halbert, L. L. Hutchings, R. Rhodes, E. I. Stiefel, *J. Am. Chem. Soc.* **1986**, *108*, 6437.
[19] J. Beck, personal communication, **1990**.
[20] L. Pauling, *Die Natur der chemischen Bindung*, 3rd ed., Verlag Chemie, Weinheim, **1976**; *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York, **1960**.
[21] *SHELXTL PLUS Program Package*, SIEMENS GmbH, Madison, WI.
[22] W. Tremel, M. Kriege, B. Krebs, G. Henkel, *Inorg. Chem.* **1988**, *27*, 3886.
[23] *International Tables for X-Ray Crystallography*; Kynoch, Birmingham, England, **1974**, vol. IV.

[126/93]