



**The crystal structure of Ni<sub>9.54</sub>Pd<sub>7.48</sub>S<sub>15</sub>.**

Dubost, Vincent; Balic Zunic, Tonci; Makovicky, Emil

*Published in:*  
Canadian Mineralogist

*Publication date:*  
2007

*Document version*  
Publisher's PDF, also known as Version of record

*Citation for published version (APA):*  
Dubost, V., Balic Zunic, T., & Makovicky, E. (2007). The crystal structure of Ni<sub>9.54</sub>Pd<sub>7.48</sub>S<sub>15</sub>. *Canadian Mineralogist*, 45, 847-855.

## THE CRYSTAL STRUCTURE OF $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$

VINCENT DUBOST<sup>§</sup>, TONČI BALIĆ-ŽUNIĆ AND EMIL MAKOVICKY<sup>¶</sup>

*Geological Institute, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen, Denmark*

### ABSTRACT

The crystal structure of the synthetic compound  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$  has been solved and refined to an R-factor of 3.3%. It belongs to the space group  $Pm\bar{3}m$ , with a cell edge  $a$  of 9.872 Å. It is isostructural with the published structures of  $\text{Pd}_{17}\text{Se}_{15}$  and  $\text{Rh}_{17}\text{S}_{15}$ . In the structure of  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , Pd is primarily concentrated in the square coordination sites, whereas nickel is concentrated in the flattened tetrahedral and regular octahedral sites. An interpretation of the structure of  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$  in terms of anion-centered polyhedra reveals features common with pentlandite. Despite the mixed character of the cationic sites, this compound does not appear to be an intermediate member of a hypothetical solid-solution  $\text{Pd}_{17}\text{S}_{15} - \text{Ni}_{17}\text{S}_{15}$ . The stability of  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$  results from the size fit of the two M–S substructures: a palladium-bearing substructure, with metal–metal bonds, and a nickel-bearing substructure. The site partitioning observed in this structure suggests a similar one for the minor elements (Cu and Hg) in natural palladseite. Because of cation coordinations, the structure is believed to be incompatible with a significant incorporation of divalent iron.

*Keywords:*  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , crystal structure,  $\text{Rh}_{17}\text{S}_{15}$  structure-type.

### SOMMAIRE

Nous avons résolu et affiné la structure du composé synthétique  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$  jusqu'à un résidu R de 3.3%. Ce composé cubique, groupe spatial  $Pm\bar{3}m$ , paramètre réticulaire  $a$  égal à 9.872 Å, est isostructural avec  $\text{Pd}_{17}\text{Se}_{15}$  et  $\text{Rh}_{17}\text{S}_{15}$ . Dans la structure de  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , le palladium est essentiellement concentré dans les sites à coordinance en plan-carré, tandis que le nickel est préférentiellement incorporé dans les sites tétraédriques aplatis et ainsi que dans le site octaédrique. Si on choisit des polyèdres centrés sur les anions, la structure montre des traits communs avec la structure de la pentlandite. Malgré le caractère mixte des sites cationiques, le composé ne semble pas être le terme intermédiaire d'une solution solide hypothétique  $\text{Pd}_{17}\text{S}_{15} - \text{Ni}_{17}\text{S}_{15}$ . Nous proposons que la stabilité de ce composé résulte de l'ajustement des paramètres des deux sous-structures M–S: la sous-structure riche en palladium, comprenant des liaisons métal–métal, et la sous-structure riche en nickel. La répartition sur les sites observée dans cette structure donnerait une indication de la répartition des éléments mineurs (Cu et Hg) dans les échantillons naturels de palladseite. A cause de la coordinance des cations, la structure est vraisemblablement inapte à incorporer le fer bivalent.

*Mots-clés:*  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , structure cristalline, type structural de  $\text{Rh}_{17}\text{S}_{15}$ .

### INTRODUCTION

The phase studied is one of the numerous synthetic compounds of platinum-group elements (PGE) prepared in the context of the phase-relation studies, primarily by means of dry synthesis (Makovicky 2002), to provide a better understanding of parageneses in magmatic ore deposits. In the work on the system Pd–Ni–S, Karup-Møller & Makovicky (1993) encountered a ternary isotropic phase in an investigation of the 550°C isotherm. Its empirical formula derived from electron-microprobe analyses was given as  $\text{Pd}_{3.81}\text{Ni}_{5.30}\text{S}_8$ . This

phase was of interest because of its position between pentlandite and a hypothetical sulfur analogue of  $\text{Pd}_{17}\text{Se}_{15}$ : which of these two structure types does it adopt? The present analysis shows it to be isostructural with  $\text{Pd}_{17}\text{Se}_{15}$  and  $\text{Rh}_{17}\text{S}_{15}$ , both known as minerals (Cabri 2002).

### DATA COLLECTION AND STRUCTURE SOLUTION

The crystal fragment used in this work is the same as that studied by Karup-Møller & Makovicky (1993).

<sup>§</sup> On research leave from the Ecole Normale Supérieure de Cachan, France. *Present address:* Institut des Nanosciences de Paris, Campus Boucicaut, Rue de Lourmel, F-75015 Paris, France.

<sup>¶</sup> *E-mail address:* emilm@geol.ku.dk

Results of their electron-microprobe chemical analysis are reproduced in Table 1.

X-ray intensity data were collected on a Bruker AXS four-circle diffractometer equipped with a SMART 1000CCD detector and a flat graphite monochromator using MoK $\alpha$  radiation from a fine-focus tube (Table 2). The SMART system of programs was used for crystal-lattice determination and X-ray data collection, SAINT+ for data reduction, including intensity integration, background and Lorentz polarization correction, and SHELXTL for the structure solution and refinement; all are Bruker AXS products. The program XPREP from the SHELX package was used to perform an empirical absorption-correction based on intensity measurements of symmetry-equivalent reflections, considering the crystal fragment studied as a triaxial ellipsoid.

No systematic extinctions have been observed. From among the five possible space-groups in the

cubic system ( $Pm\bar{3}$ ,  $P23$ ,  $Pm\bar{3}m$ ,  $P\bar{4}3m$ , and  $P432$ ), the structure solution was first attempted in  $Pm\bar{3}$  because the statistical value  $|E^2 - 1| = 1.095$  suggested a centrosymmetric space-group. The structure was solved by direct methods, and difference-Fourier syntheses were used in subsequent refinements. Results of these refinement cycles revealed that the structure does not deviate from the space group  $Pm\bar{3}m$ ; the compound is isostructural with palladseite Pd<sub>17</sub>Se<sub>15</sub> (Geller 1962). Thus, the refinement has been completed in the space group  $Pm\bar{3}m$ .

In the second stage of refinement, the occupancies of the metal sites were refined. The difference in scattering factor of Ni versus Pd allows us to refine the occupancy factor for nickel and palladium at each site, assuming full occupancies of all cation sites. The final refinement was performed using anisotropic displacement-parameters for all positions and an allowance for secondary extinction. Attempts at a refinement with separate coordinates for Ni and Pd atoms at the same structural site did not improve the R factors, and the differences in coordinates were insignificant (atoms less than 0.1 Å apart). In the last refinement, equal coordinates and displacement factors of Ni and Pd atoms were used in each mixed site. The highest positive maximum in the difference-Fourier synthesis was 4.16 e/Å<sup>3</sup> at the fractional coordinates (0, ½, ½), in the center of the scallop-like [M<sub>14</sub>S<sub>10</sub>] polyhedron (see under Description of the Polyhedra further below), and the lowest negative one was -2.71 e/Å<sup>3</sup>, coincident with Ni1. Fractional coordinates are listed in Table 3, and anisotropic displacement parameters are given in Table 4. A table of structure-factors is available from the Depository of Unpublished Data on the MAC web site [document Ni-Pd-S, CM45\_847].

TABLE 1. CHEMICAL COMPOSITION

		Ni	Pd	S	total	formula
(1a)	wt.%	32.47	42.28	26.75	101.58	Ni <sub>9.93</sub> Pd <sub>7.14</sub> S <sub>15</sub>
	at.%	30.99	22.27	46.74		
(1b)	wt.%	30.40	43.37	26.23	100	Ni <sub>9.54</sub> Pd <sub>7.46</sub> S <sub>15</sub>
	at.%	29.64	23.48	46.87		

(1a) Results of electron-microprobe analysis (Karup-Møller & Makovicky 1993).  
(1b) Results of X-ray structure refinement, calculated on the basis of 32 atoms (this study).

TABLE 2. EXPERIMENTAL DATA FOR Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub>

Crystal data			
Chemical formula	Ni <sub>9.54</sub> Pd <sub>7.46</sub> S <sub>15</sub>	No. of reflections	779
<i>Mr</i>	906.40	for cell parameters	
System, space group	Cubic, $Pm\bar{3}m$	$\theta$ range (°)	4.6–35.5
<i>a</i> (Å)	9.8717(3)	$\mu$ (mm <sup>-1</sup> )	17.50
<i>V</i> (Å <sup>3</sup> )	962.00(5)	Temperature (K)	298 (2)
<i>Z</i>	4	Crystal form, color	Platy, black
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	6.258	Crystal size (mm)	0.11 × 0.11 × 0.04
Radiation type	MoK $\alpha$		
Data collection			
Diffractometer	Smart 1000 CCD		
Absorption correction	Empirical (from intensities of equivalent reflections)		
<i>T<sub>min</sub></i>	0.100	<i>T<sub>max</sub></i>	0.208
No. of measured, independent and observed reflections			13478, 515, 401
Criterion for observed reflections		<i>I</i> > 2 $\sigma$ ( <i>I</i> )	
<i>R<sub>int</sub></i>	0.094	$\theta_{max}$ (°)	36.2
Range of <i>h, k, l</i>	-15 - <i>h</i> - +15	-15 - <i>k</i> - +16	-16 - <i>l</i> - +16
Refinement			
Refinement on	<i>F</i> <sup>2</sup>		
R [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> ), <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>		0.033, 0.089, 1.11	
No. of relections	515 reflections	No. of parameters	29
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 1.3631P]$ , where $P = (F_o^2 + 2F_c^2)/3$		
( $\Delta\sigma$ ) <sub>max</sub>	0.266	$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>3</sup> )	4.16, -2.71
Extinction method	SHELXL	Extinction coefficient	0.0012(2)

TABLE 3. POSITIONAL AND OCCUPANCY PARAMETERS FOR Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub>

Mixed site	Atom	s.o.f.	multi- plicity	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
M1	Ni1	0.614(4)	24	0.1483(1)	0.35176(4)	0.35176(4)	0.0117(2)
	Pd1	0.386(4)					
M2	Pd2	0.499(5)	6	0.00000	0.2333(1)	0.00000	0.0095(3)
	Ni2	0.501(5)					
M3	Pd3	0.860(7)	3	0.00000	0.50000	0.00000	0.0100(3)
	Ni3	0.140(7)					
M4	Ni4	0.91(1)	1	0.50000	0.50000	0.50000	0.0130(9)
	Pd4	0.09(1)					
	S1	1.0	12	0.1725(1)	0.50000	0.1725(1)	0.0121(4)
	S2	1.0	12	0.00000	0.2298(1)	0.2298(1)	0.0100(4)
	S3	1.0	6	0.2562(3)	0.50000	0.50000	0.0135(5)

s.o.f.: site-occupancy factor.

## DESCRIPTION OF THE STRUCTURE

The refined structure has four distinct cation sites, all of which were refined as mixed (Pd,Ni) sites, and three distinct sulfur positions. All cation sites are in different types of special positions, with 2, 1, and 0 degrees of freedom, respectively, for positional parameters. The sites were labeled according to the scheme of labeling

used for Pd<sub>17</sub>Se<sub>15</sub> by Geller (1962a). The cation sites are labeled as M1 to M4 (Fig. 1) because of their mixed character.

*The cation polyhedra: the M1 site*

The coordination of M1 can either be described as strongly distorted square-planar, where the arrangement of four S atoms deviates from planarity, or as a strongly deformed tetrahedron, flattened along one of the  $\bar{4}$  axes (Fig. 2). This causes an increase of the S2–M1–S3 and S1–M1–S1 angles to a value near 160°, and a decrease of the S1–M1–S2 and S1–M1–S3 angles to nearly 90°, to be compared with the regular square-planar coordination for which these angles are equal to 180° and 90°, respectively. In the real structure, the S2–M1–S3 and S1–M1–S1 angles, as well as the S1–M1–S2 and S1–M1–S3 angles, differ from one another, indicating that the compression does not preserve the  $\bar{4}$  axis exactly. The M1–S3 bond is lengthened, and the M1–S2 bond is shortened, in comparison to the M1–S1 bonds.

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS FOR Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub>

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
M1	0.0132(3)	0.0110(2)	0.0110(2)	0.0019(2)	-0.0027(1)	-0.0027(1)
M2	0.0090(3)	0.0107(4)	0.0090(3)	0.00000	0.00000	0.00000
M3	0.0105(4)	0.0092(5)	0.0104(4)	0.00000	0.00000	0.00000
M4	0.0130(1)	0.0130(1)	0.0130(1)	0.00000	0.00000	0.00000
S1	0.0123(5)	0.0115(7)	0.0123(5)	0.00000	-0.0023(6)	0.00000
S2	0.0114(7)	0.0118(5)	0.0118(5)	0.0010(6)	0.00000	0.00000
S3	0.010(1)	0.0151(7)	0.0151(7)	0.00000	0.00000	0.00000

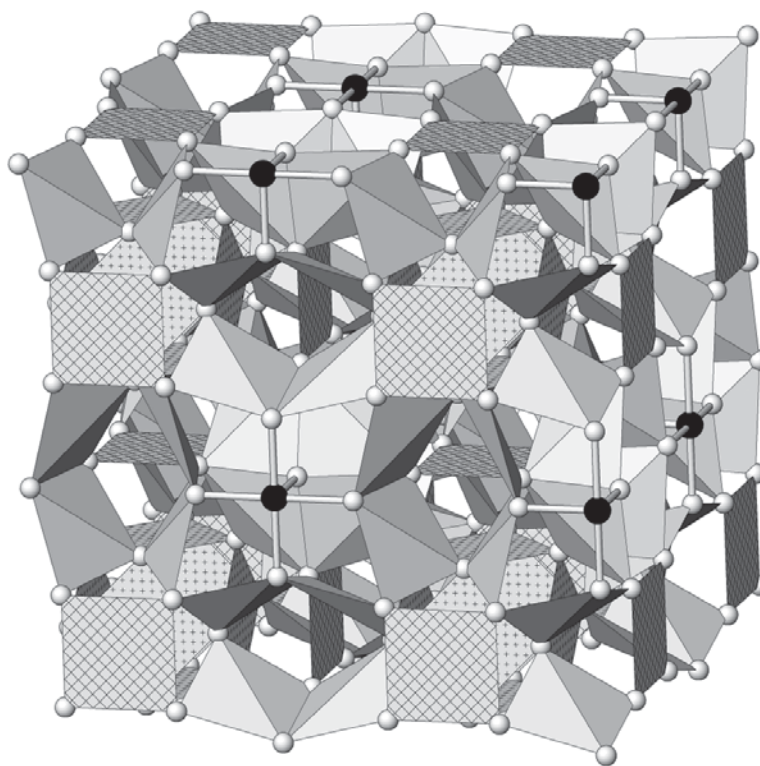


FIG. 1. Crystal structure of Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub>. The coordination polyhedra of M1 are left uncolored, those of M2 are decorated by a pattern of crosses, M3 are cross-hatched, and M4 expressed in a ball-and-stick form. The M4 sites define the vertices of the unit cell.

Consequently, the only symmetry element preserved in the flattened tetrahedron is the S2–M1–S3 mirror plane. Table 5 presents the geometrical characteristics of this polyhedron.

The degree of “flattening” of the tetrahedron, or the complementary degree of “tetrahedral distortion” of the square-planar coordination, can be calculated by the following formalism. Let  $h$  represent the height of the tetrahedron along the axis of “flattening”. Its value can be calculated for a group of the four atoms defining the distorted tetrahedron or square if a plane is fitted to the group by a least-squares procedure. The average absolute deviation of the atoms from this plane is calculated, and the double value is assumed to represent  $h$ . Let  $a$  be the edge of the tetrahedron or square (or the average value for a distorted group). For an ideal tetrahedron  $h = a / \sqrt{2}$ , whereas for a plane,  $h$  is equal to 0. The percentage of tetrahedral distortion of the square-planar coordination is then  $100 \cdot h \sqrt{2} / a$  %, with the 100% distortion corresponding to an ideal tetrahedron, whereas the complementary degree of flattening (in %) can be calculated as  $100 \cdot (1 - h \sqrt{2} / a)$  %, with the 100% flattened tetrahedron corresponding to an ideal square planar coordination. This procedure yields 74% flattening for the M1 polyhedron.

Various flattened tetrahedra are also encountered in many nickel or palladium chalcogenides or pnictides like PdS, PdSe,  $\text{La}_6\text{Ni}_6\text{P}_{17}$  and the isostructural compounds  $\text{Rh}_{17}\text{S}_{15}$  (miassite; cf. Cabri 2002) and  $\text{Pd}_{17}\text{Se}_{15}$  [palladseite (Davis *et al.* 1977)] (Table 6). The situation closest to  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$  is observed in  $\text{Pd}_{17}\text{Se}_{15}$  (Geller 1962a) and  $\text{Rh}_{17}\text{S}_{15}$  (Geller 1962b), where the values of the coefficient of flattening, 76% and 77%, respectively, are very close to the value calculated for  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ . All coordination polyhedra of this type mentioned above have a degree of flattening greater than 50%, and are therefore quantitatively closer to the square planar coordination than to a tetrahedral one. The Ni1 atom in  $\text{La}_6\text{Ni}_6\text{P}_{17}$  (Braun & Jeitschko 1978) is closest to the tetrahedral coordination; with 57% flattening, it is practically midway between a tetrahedral and a planar one. The most planar sites are found in PdSe and PdS (about 90% flattening), in accordance with the coordination preferences of Pd, discussed later. However, although Ni predominates at the M1 site (60% Ni) in  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , the flattening of its coordination tetrahedron is very close to the one observed for pure Pd and Rh sites in the isostructural palladseite and miassite. This shows that the degree of flattening also depends on the structure type of the compound.

#### The M2 and M3 sites

The M2S<sub>2</sub> coordination is a nearly regular square. The metal atom is shifted out of its plane only by 0.03 Å, along the (100) direction, perpendicular to the square, and out of the cuboctahedron formed by the six M2 coordination squares, and toward the adjacent

M3 site (Fig. 1). This small shift of the M2 atom might be a consequence of a strong metal–metal interaction between M2 and M3.

The occupancy of the M2 site is 50 at.% Pd and 50 at.% Ni, and the M2–S2 distance lies within the range of metal–sulfur bond distances for Pd and Ni in square-planar coordination (Tables 5, 6).

The M3S<sub>4</sub> coordination is a regular square, in which the central atom is positioned in the center of the S<sub>4</sub> group. This site contains 86 at.% Pd and 14 at.% Ni. The M3–S1 distance is larger than the usual distances encountered for palladium in square-planar coordination with sulfur (Table 6). The same trend is observed for the corresponding Pd3–Se and Rh3–S distances in  $\text{Pd}_{17}\text{Se}_{15}$  and  $\text{Rh}_{17}\text{S}_{15}$ . In arsenohauchecornite,  $(\text{As}_{0.5}\text{Bi}_{0.5})(\text{Ni}, \text{Bi})\text{Ni}_8\text{S}_8$  (Grice & Ferguson 1989), nickel is in the center of a slightly elongate square formed by S atoms with Ni–S distances, 2.26 to 2.38 Å, also longer than usual for Ni–S in the square coordination. The complete coordination-sphere of nickel also includes two bismuth atoms at 2.71 Å. This is equivalent to the situation in the structure type examined here, where M3 forms two metal–metal bonds with adjacent M2 sites (2.63 Å in  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ ). The longer metal–anion bonds in the square-planar coordination could therefore be a consequence of the formation of two additional metal–metal bonds.

TABLE 5. COORDINATION CHARACTERISTICS OF M SITES IN  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$

	S2	S1	S1	S3		
M1						
S2	2.245(1)	89.8(0)	89.8(0)	166.5(1)		
S1	3.214(1)	2.309(1)	163.9(1)	92.1(1)		
S1	3.214(2)	4.573(1)	2.309(1)	92.1(1)		
S3	4.541(2)	3.337(1)	3.337(1)	2.327(1)		
M2						
S2	2.269(1)	178.3(1)	90.0(1)	90.0(1)		
S2	4.538(2)	2.269(1)	90.0(1)	90.0(1)		
S2	3.209(1)	3.209(1)	2.269(1)	178.3(1)		
S2	3.209(1)	3.209(1)	4.538(1)	2.269(1)		
M3						
S1	2.408(1)	90.0(0)	180.0(0)	90.0(0)		
S1	3.405(2)	2.408(1)	90.0(0)	180.0(0)		
S1	4.816(2)	3.405(2)	2.408(1)	90.0(0)		
S1	3.405(2)	4.816(2)	3.405(2)	2.408(1)		
M4						
S3	2.408(3)	180.0(1)	90.0(1)	90.0(1)	90.0(1)	90.0(1)
S3	4.815(4)	2.408(3)	90.0(1)	90.0(1)	90.0(1)	90.0(1)
S3	3.405(3)	3.405(3)	2.408(3)	180.0(1)	90.0(1)	90.0(1)
S3	3.405(3)	3.405(3)	4.815(3)	2.408(3)	90.0(1)	90.0(1)
S3	3.405(3)	3.405(3)	3.405(3)	3.405(3)	2.408(3)	180.0(1)
S3	3.405(3)	3.405(3)	3.405(3)	3.405(3)	4.815(3)	2.408(3)

In the coordination tables, the diagonal contains the bond distances, the upper right-hand triangle contains the bond angles, whereas the lower left-hand triangle contains the ligand–ligand distances. Distances are in Å.

*The M4 site*

The only octahedral site in the structure (Fig. 2) is occupied nearly completely by pure nickel, with only 9 at.% Pd, and it is a perfectly regular octahedron (Table 5). In Table 6, the M4–S3 distance is compared with Ni–S distances observed in octahedral coordination with sulfur.

*Polyhedral description of the structure*

The structure of Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub> is a complex framework formed by the three types of cation-centered coordination polyhedra described: the M4 octahedron, a severely flattened tetrahedron (*i.e.*, a distorted square coordination) of M1, and square-planar coordinations of M2 and M3. It can be understood as a combination of two component structures.

The first component contains the octahedra and the flattened tetrahedra. The M4S<sub>6</sub> octahedron shares each of its S3 vertices with four flattened tetrahedra,

M1S<sub>2</sub>S1S3S1, the latter being linked together into a tetramer by sharing their S3–S1 edges (Fig. 2). In this way, a sort of an “exploded” cube is formed around the central octahedron, with the center of each face occupied by the S3 vertex of the octahedron, and decorated by a tetramer (Fig. 2). The tetramers show a concave and a convex side; the convex one faces the octahedron, whereas the concave side faces a mirror plane. Two mirror-related tetramers form a scallop-like polyhedron by sharing common S2 atoms (Fig. 3a). In this way, <100> rows of alternating octahedra and “scallops” are formed (Fig. 3a). The situation resembles that in pentlandite, where each cation-centered octahedron is surrounded by six “*stella octangula*” clusters of eight tetrahedra (O’Keeffe & Hyde 1996) (Fig. 3b). The configuration of a “scallop” in Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub>, however, is quite different from the configuration of the *stella octangula*. Moreover, the full structure of Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub> is formed as an interpenetration of this component with the one described below, whereas the structure of pentlandite consists only of octahedra and *stellae octangulae*.

The second component consists of the rows of coordination squares of M2 and M3. They share the S1 and S2 atoms with the first component. The substructure of the second component can be described as rods ...M3–M2–M2–M3–... parallel to crystal axes. The coordination squares of M2 and M3 are mutually rotated by 45° if seen along the rod axis, and are interconnected by short M2–M3 metal bonds. The bonding in the rods follows a similar mechanism as the one occurring in the Pt(CN)<sub>4</sub> chain compounds, which are known for their one-dimensional metal–metal bonding.

Around the points of intersection, the M2S<sub>2</sub> squares of all three rod orientations share the S2 atoms, forming an M<sub>2</sub>S<sub>2</sub> cuboctahedron (Fig. 1). A similar kind of cuboctahedron is found in the structure of PdCl<sub>2</sub> (Belli Dell’Amico *et al.* 1996). Figure 1 illustrates the interpenetration of the intersecting, rod-like portions with M2 and M3 and the robust octamer scallops with intervening octahedra.

*The coordination of anions*

The compound Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub> is a subsulfide, with a proportion of cations in the formula higher than suggested by their lowest valences (2+ in this case); it has direct Pd–Pd interactions. Makovicky (2002, 2006) demonstrated that a structural description of subsulfides and selenides of Pd by means of anion-centred coordination polyhedra gives a much clearer picture of structural configurations than the description based on the coordination polyhedra of cations. As a consequence, a short description of the present compound in these terms will be given here.

The sulfur sites S1 and S3 have a square-pyramidal coordination similar to the SN<sub>5</sub> pyramids in millerite (Rajamani & Prewitt 1974) and the SM<sub>5</sub> pyramids

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) IN Ni AND Pd CHALCOGENIDES

A. Ni-S distances in NiS <sub>6</sub> coordination octahedra			
Ni <sub>9.54</sub> Pd <sub>7.46</sub> S <sub>15</sub>		this study	2.408 Å
Vaesite NiS <sub>2</sub> (pyrite type)		Nowack <i>et al.</i> (1991)	2.391
NiS (nickeline type)		Trahan <i>et al.</i> (1970)	2.394
Ba <sub>3</sub> Ni <sub>27</sub> S <sub>27</sub>		Gelabert <i>et al.</i> (1997)	2.390
NiV <sub>2</sub> S <sub>4</sub>		Murugesan <i>et al.</i> (1982)	2.379
B. Metal–chalcogen distances for Ni and Pd in square-planar coordination			
PdS	Brese <i>et al.</i> (1985)	Pd1	2.340 Å
		Pd2	2.320
		Pd3	2.340
PdSe	Ijjaali & Ibers (2001)	Pd1	2.46
		Pd2	2.42
		Pd3	2.43
PdS <sub>2</sub>	Gronvold & Rost (1957)		2.30
PdSe <sub>2</sub>			2.44
K <sub>2</sub> Pd <sub>5</sub> S <sub>4</sub>	Huster & Bronger (1974)		2.34
K <sub>2</sub> Pd <sub>3</sub> Se <sub>4</sub>	Bronger <i>et al.</i> (1991)		2.47
Ni <sub>9.54</sub> Pd <sub>7.46</sub> S <sub>15</sub>	this study	M2	2.27
		M3	2.41
Pd <sub>17</sub> Se <sub>15</sub>	Geller (1962a)	Pd2	2.44
		Pd3	2.52
K <sub>2</sub> Ni <sub>3</sub> S <sub>2</sub>	Elder <i>et al.</i> (1996)		2.22
Cs <sub>2</sub> Ni <sub>3</sub> Se <sub>4</sub>	Bronger <i>et al.</i> (1991)		2.34
C. Metal–metal distances			
Pd <sub>17</sub> Se <sub>14</sub>	Geller (1962a)	Pd2–Pd3	2.78 Å
Pd metal	King & Manchester (1978)		2.75
Rh <sub>17</sub> S <sub>15</sub>	Geller (1962b)	Rh2–Rh3	2.59
Rh metal	Swanson & Ugrinic (1954)		2.69
Ni <sub>9.54</sub> Pd <sub>7.46</sub> S <sub>15</sub>	this study	M2–M3	2.63*
Ni metal	Swanson & Tatge (1953)		2.49

\* Site-occupancy factors for M2 are Pd 0.50 and Ni 0.50; for M3, they are Pd 0.86, Ni 0.14.



in pentlandite (Rajamani & Prewitt 1975). Both sites have a configuration close to a square pyramid with a maximum volume, with the height approximately equal to the length of the edge of the pyramidal base (Makovicky & Balić-Žunić 1998) (Fig. 4). Atom S2

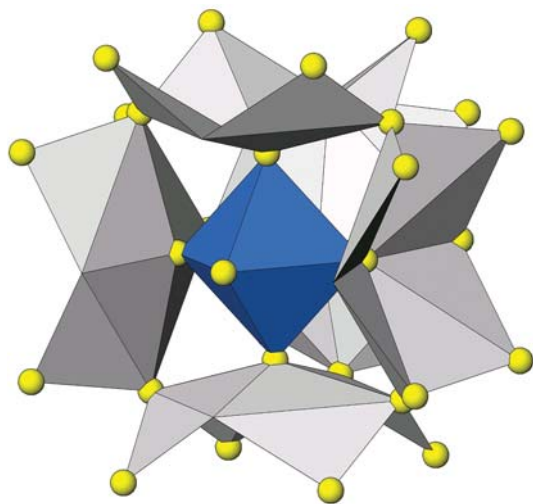


FIG. 2. Six “scallop shells”, composed of edge-sharing tetramers of flattened tetrahedra of M1 surrounding a central M4 octahedron in  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ . The front tetramer has been omitted in order to reveal the central octahedron.

has an elongate, disphenoidal coordination with a considerable distortion (11.7% volume-based distortion, Makovicky & Balić-Žunić 1998) from an ideal tetrahedron. No short S–S distances have been observed; the shortest distances of 3.21 Å are forced by the coordinations of adjacent cations. The S coordinations in the examined structure are much closer to the polyhedra with a maximum volume than those of the cations (the majority of the latter are close to a square-planar form). We consider this an important factor for the stability of the structure.

Four  $\text{S1M1}_3\text{M3}$  square pyramids, linked together by sharing the M3 apex, produce a “maltese cross” (Fig. 4). Six  $\text{S3M1}_4\text{M4}$  square pyramids share the M4 apex, producing a “three-dimensional maltese cross” (Fig. 4). The latter configuration of polyhedra is also observed in pentlandite, where the shared cation is the octahedral cation. The outer shape of this grouping is a rhombicuboctahedron defined by 24 M1 atoms. The remaining voids of the structure are filled by an aggregate of twelve elongate tetrahedra  $\text{S2M}_2\text{M1}_2$  around a central  $\text{M2}_6$  octahedral void; the outer shape of this grouping, also defined by 24 M1 atoms, is a truncated cube (Fig. 4). The description of the structure of palladseite ( $\text{Pd}_{17}\text{Se}_{15}$ ) in these terms was already given by O’Keeffe & Hyde (1996). Packing of rhombicuboctahedra in pentlandite is much more compact than in  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , with regular  $\text{SM}_4$  tetrahedra as the only interstitial element. This description is the most succinct definition of the difference between these two

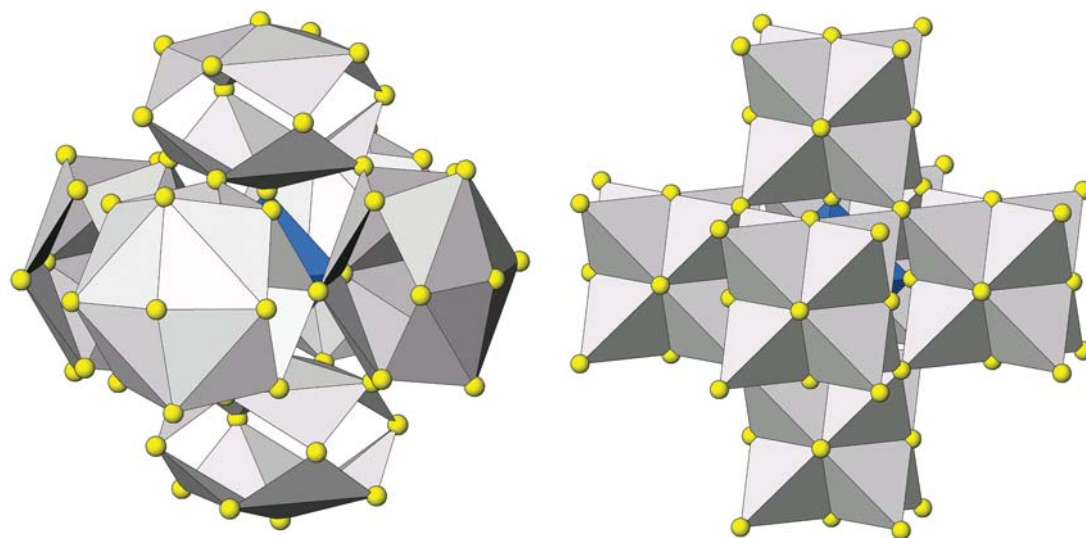


FIG. 3. (a) Complete scallop-shaped octamers of coordination tetrahedra of M1 surrounding a coordination octahedron of M4 in  $\langle 100 \rangle$  directions of the cubic cell of  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ . (b) “Stella octangula” octamers of edge-sharing tetrahedra surrounding a cation in octahedral coordination in  $\langle 100 \rangle$  directions of the cubic cell in the structure of pentlandite.

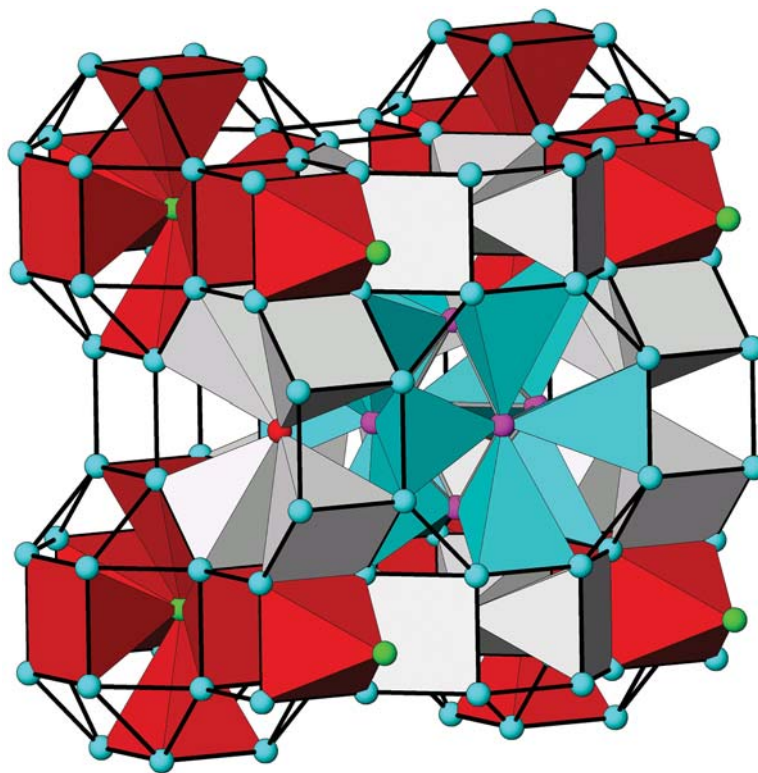


FIG. 4. Anion polyhedra in  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ . Four-fold “maltese crosses” of S1-based coordination polyhedra are uncolored; six-fold maltese crosses of S3-based polyhedra are red, and S2-centered elongate tetrahedra are blue. Rhombicuboctahedra and cuboctahedra are outlined by bold lines.

compositionally similar cubic minerals with similar values of the lattice parameter.

#### DISCUSSION

Given the absence of anion pairing in  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , the oxidation state of sulfur is  $-2$ , and the average oxidation state for nickel and palladium is  $+1.76$ , very close to  $+2$ . The difference results from M–M bonding present in the structure. Although the phase studied is a “moderate” subsulfide, the complicated coordination-polyhedra formed by Pd and minor S around each Pd in the other subsulfides (*cf.* Makovicky 2002, 2006) are missing.

In “normal” sulfides with the M:S ratio equal to or smaller than one, the  $4d^8$  element palladium ( $\text{Pd}^{2+}$ ) exhibits almost exclusively a spin-paired square-planar coordination, contrary to the  $3d^8$  element, nickel ( $\text{Ni}^{2+}$ ), which can exhibit square planar, tetrahedral, pyramidal and high-spin octahedral coordination. The case of  $\text{CsNiPdF}_5$ , where  $\text{Ni}^{2+}$  is found only octahedrally

coordinated and  $\text{Pd}^{2+}$  is found only in square-planar coordination, provides an example of this difference in chemical behavior (Ruchaud *et al.* 1993). In full agreement with the above, in the case of  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ , we find a preferential occupancy of the square and nearly-square sites by palladium atoms, and especially of the position M3 with two metal–metal interactions.

According to Karup-Møller & Makovicky (1993), the phase studied shows little variation in composition, although the solubility of nickel in the associated PdS is rather important (nearly 10 at.%). Although this study shows the mixed character of metal sites, analogous hypothetical phases  $\text{Ni}_{17}\text{S}_{15}$  and  $\text{Pd}_{17}\text{S}_{15}$  are not known, and  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$  does not appear to be an intermediate member of a hypothetical solid-solution  $\text{Ni}_{17}\text{S}_{15} - \text{Pd}_{17}\text{S}_{15}$  with an extensive  $\text{Ni} \leftrightarrow \text{Pd}$  substitution. We propose a structural explanation for the restricted domain of compositional stability of  $\text{Ni}_{9.54}\text{Pd}_{7.46}\text{S}_{15}$ . Given the fact that an isostructural Pd-bearing compound is known with selenium, which is larger than sulfur, and the isostructural S-bearing



compound is known with rhodium, with an ionic radius smaller than that of palladium, the (relative) size of cations and anions that leads to a formation of interatomic distances appropriate for the types of interactions observed is of importance for the stability of the structure. Given the differences in site occupancies of the two components defined above, the “decorated cubes” that concentrate Ni, and the “intersecting rods” enriched in Pd, which result from different preferences in coordination of Pd and Ni, the restricted compositional field results from a balance between the dimensions of these two substructures. An increase in the content of palladium, which will preferably occupy the square coordination sites of the “intersecting rods”, would cause an increase of the M2–M3 distances, without being appropriately compensated by an increase of the size of the “decorated cubes” of M1 and M4 polyhedra. On the other hand, further increase in the content of nickel, which is expected to concentrate in the flattened tetrahedra and the central octahedron, would cause a decrease in the size of the “decorated cubes”, without an appropriate decrease of the M2–M3 distance in the palladium-bearing “intersecting rods”. Consequently, the observed occupancies of the cation sites appear to stabilize the structure. Compensation of potential differences in thermal expansion of “decorated cubes” and “intersecting rods” by Ni–Pd substitution might lead to deviations from the composition studied at temperatures different from 550°C.

The natural samples of palladseite contain a significant amount of copper and mercury (Cabri 2002). Studies of Cu- and Hg-doped Pd<sub>17</sub>Se<sub>15</sub> are necessary to investigate the site partitioning analogous to that observed in Ni<sub>9.54</sub>Pd<sub>7.46</sub>S<sub>15</sub>, and to determine the preferred sites chosen by copper and mercury in this structure type. The system Pd–Cu–Se is actually under investigation by means of dry syntheses by Makovicky & Karup-Møller. The phase studied was not synthesized in the quaternary system Pd–Fe–Ni–S (Makovicky & Karup-Møller 1995, Makovicky 2002), in agreement with the paucity of regular tetrahedra and octahedra suitable for Fe in its structure. Therefore, we assume that it ought to be absent in the mixed, Pd–Ni–Fe assemblages in nature.

#### ACKNOWLEDGEMENTS

This research was financed by the Carlsberg Foundation, Denmark (project no. 57248). V.D. thanks the Ecole Normale Supérieure de Cachan (France) for the leave and support granted. The qualified assistance of Mrs. Camilla Sarantaris, Mr. H. Sinh and the keen interest of Dr. S. Karup-Møller as well as the colorful review of the first version of this manuscript by Dr. A.M. McDonald were appreciated.

#### REFERENCES

- BALIĆ-ŽUNIĆ, T. & MAKOVICKY, E. (1996): Determination of the centroid or “best centre” of a coordination polyhedron. *Acta Crystallogr.* **B52**, 78-81.
- BALIĆ-ŽUNIĆ, T. & VICKOVIĆ, I. (1996): IVTON – program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. *J. Appl. Crystallogr.* **29**, 305-306.
- BELLI DELL'AMICO, D., CALDERAZZO, F., MARCHETTI, F. & RAMELLO, S. (1996): Molecular structure of Pd<sub>6</sub>Cl<sub>12</sub> on single crystals chemically grown at room temperature. *Angew. Chem.* **35**, 1331-1333.
- BRAUN, D.J. & JEITSCHKO, W. (1978): The synthesis and crystal structure of the polyphosphides La<sub>6</sub>Ni<sub>6</sub>P<sub>17</sub>, Ce<sub>6</sub>Ni<sub>6</sub>P<sub>17</sub> and Pr<sub>6</sub>Ni<sub>6</sub>P<sub>17</sub>. *Acta Crystallogr.* **B34**, 2069-2074.
- BRESE, N.E., SQUATTRITO, P.J. & IBERS, J.A. (1985): Reinvestigation of the structure of PdS. *Acta Crystallogr.* **C41**, 1829-1830.
- BRONGER, W., RENNAU, R. & SCHMITZ, D. (1991): Schichtstrukturen ternärer Chalkogenide A<sub>2</sub>M<sub>3</sub>X<sub>4</sub> (A = K, Rb, Cs; M = Ni, Pd, Pt; X = S, Se). *Z. Anorg. Allg. Chem.* **597**, 27-32.
- CABRI, L.J., ed. (2002): The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-group Elements. *Can. Inst. Mining, Metall., Petroleum, Spec. Vol.* **54**.
- DAVIS, R.J., CLARK, A.M. & CRIDDLE, A.J. (1977): Palladseite, a new mineral from Itabira, Minas Gerais, Brazil. *Mineral. Mag.* **41**, 123.
- ELDER, S.H., JONICK, S., BREC, R., GELABERT, M.C. & DISALVO, F.J. (1996): Structural and electronic properties of K<sub>2</sub>Ni<sub>3</sub>S<sub>4</sub>, a pseudo-two dimensional compound with a honeycomb-like arrangement. *J. Alloys Compd.* **235**, 135-142.
- GELABERT, M.C., HO, M.H., MALIK, A.-S., DISALVO, F.J., DENIARD, P. & BREC, R. (1997): Structure and properties of Ba<sub>6</sub>Ni<sub>25</sub>S<sub>27</sub>. *Chemistry* **3**, 1884-1889.
- GELLER, S. (1962a): The crystal structure of Pd<sub>17</sub>Se<sub>15</sub>. *Acta Crystallogr.* **15**, 713-721.
- GELLER, S. (1962b): The crystal structure of the superconductor Rh<sub>17</sub>S<sub>15</sub>. *Acta Crystallogr.* **15**, 1198-1201.
- GRICE, J.D. & FERGUSON, R.B., (1989): The crystal structure of arsenohauchecornite. *Can. Mineral.* **27**, 137-142.
- GRONVOLD, F. & ROST, E. (1957): The crystal structure of PdSe<sub>2</sub> and PdS<sub>2</sub>. *Acta Crystallogr.* **10** 329-331.
- HUSTER, J. & BRONGER, W. (1974): Die Struktur von K<sub>2</sub>Pd<sub>3</sub>S<sub>4</sub> und Rb<sub>2</sub>Pd<sub>3</sub>S<sub>4</sub>. *J. Solid State Chem.* **11**, 254-260.

- IJJAALI, I. & IBERS, J.A. (2001): Crystal structure of palladium selenide, PdSe. *Z. Kristallogr.* **216**, 485-486.
- KING, H.W. & MANCHESTER, F.D. (1978): A low-temperature X-ray diffraction study of Pd and some Pd-H alloys. *J. Phys.* **F8**, 15-26.
- KARUP-MØLLER, S. & MAKOVICKY, E. (1993): The system Pd-Ni-S at 900°, 725°, 550°, and 400°C. *Econ. Geol.* **88**, 1261-1268.
- MAKOVICKY, E. (2002) : Experimental studies of palladium containing systems and compounds. *Bol. Soc. Esp. Mineral.* **25**, 5-37.
- MAKOVICKY, E. (2006): Crystal structures of sulfides and other chalcogenides. In *Sulfide Mineralogy and Geochemistry* (D.J. Vaughan, ed.). *Rev. Mineral. Geochem.* **61**, 7-125.
- MAKOVICKY, E. & BALIČ-ŽUNIČ, T. (1998): New measure of distortion for coordination polyhedra. *Acta Crystallogr.* **B54**, 766-773.
- MAKOVICKY, E. & KARUP-MØLLER, S. (1995): The system Pd-Fe-Ni-S at 900 and 725°C. *Mineral. Mag.* **59**, 685-702.
- MURUGESAN, T., RAMESH, S., GOPALAKRISHNAN, J. & RAO, C.N.R. (1982): Ternary vanadium sulphides. *J. Solid State Chem.* **44**, 119-125.
- NOWACK, E. SCHWARZENBACH, D. & HAHN, T. (1991): Charge densities in CoS<sub>2</sub> and NiS<sub>2</sub> (pyrite structure). *Acta Crystallogr.* **B47**, 650-659.
- O'KEEFFE, M. & HYDE, B.G. (1996) *Crystal Structures. 1. Patterns and Symmetry*. Mineralogical Society of America, Washington, D.C.
- RAJAMANI, V. & PREWITT, C.T. (1974): Crystal structure refinement of millerite. *Can. Mineral.* **12**, 253-257.
- RAJAMANI, V. & PREWITT, C.T. (1975): Refinement of the structure of Co<sub>9</sub>S<sub>8</sub>. *Can. Mineral.* **13**, 75-78.
- RUCHAUD, N., GRANNEC, J., TRESSAUD, A. & GRAVEREAU, P. (1993): X-ray powder structure determination and magnetic behavior of CsNiPdF<sub>5</sub>. *Mater. Lett.* **17**, 287-291.
- SWANSON, H.E. & TATGE, E. (1954): Standard X-ray diffraction powder patterns. *U.S. Nat. Bureau Standards, Circ.* **359**, 1-95.
- SWANSON, H.E. & UGRINIC, G.M. (1954): Standard X-ray diffraction powder patterns. *U.S. Nat. Bureau Standards, Circ.* **539**, 1-75.
- TRAHAN, J., GOODRICH, R.G. & WATKINS, S.F. (1970): X-ray diffraction measurements on metallic and semiconducting hexagonal NiS. *Phys. Rev. B, Solid State, Ser. 3*, **2**, 2859-2862.

Received February 2, 2005, revised manuscript accepted February 28, 2007.