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STOICHIOMETRY, STRUCTURE AND TWINNING OF GODLEVSKITE AND SYNTHETIC LOW-TEMPERATURE Ni-EXCESS NICKEL SULFIDE

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ABSTRACT

New electron-microprobe data for godlevskite from Noril'sk indicate a 9:8 (metal:sulfur) stoichiometry, consistent with the recent determination of its structure in space group *C*222, and a formula of $(Ni_{8.7}Fe_{0.3})S_8$. Powder-diffraction intensity data confirm that low-temperature Ni-excess nickel sulfide is the synthetic equivalent of godlevskite, and also has a formal composition of Ni_9S_8; α-Ni_7S_6 disproportionates on annealing at 297°C to Ni_9S_8 and Ni_3S_2. The twin law for godlevskite from Noril'sk is established as: composition plane (101), twin axis normal to (101). The structure of godlevskite and synthetic Ni_9S_8 is a hybrid of the structural elements of pentlandite, millerite and α-Ni_7S_6; unlike millerite, α-Ni_7S_6 and heazlewoodite, the structure does not contain 3-fold clusters (Ni_3) of short Ni–Ni distances.

Keywords: godlevskite, Ni-excess nickel sulfide, Ni_9S_8, twinning, crystal structure, Noril'sk.

SOMMAIRE

De nouvelles données sur la godlevskite de Noril'sk, obtenues par microsonde électronique,indiquent une stoechiométrie de neuf atomes de métal pour huit de soufre. Ces données sont en bon accord avec une détermination récente de sa structure cristalline dans le groupe spatial *C*222, et de la formule chimique, $(Ni_{8.7}Fe_{0.3})S_8$. Les maxima d'intensité dans le cliché de diffraction (méthode des poudres) confirment que le sulfure de nickel de basse température, à surplus de nickel, constitue l'équivalent synthétique de la godlevskite, et possède aussi la formule chimique Ni_9S_8; le composé α-Ni_7S_6, recuit, se décompose à 297°C en Ni_9S_8 + Ni_3S_2. On a établi la loi de macle de la godlevskite de Noril'sk: plan de composition (101), axe de la macle perpendiculaire à (101). La structure de la godlevskite et du composé synthétique Ni_9S_8 contient certains éléments structuraux de la pentlandite, millerite et α-Ni_7S_6. Contrairement aux cas de la millerite, α-Ni_7S_6 et heazlewoodite, la structure ne contient pas de groupements de trois atomes de nickel (Ni_3) possédant des distances Ni–Ni courtes.

(Traduit par la Rédaction)

Mots-clés: godlevskite, sulfure de nickel à surplus de Ni, Ni_9S_8, macle, structure cristalline, Noril'sk.

INTRODUCTION

Study of the stoichiometry, symmetry and phase relations of the Ni-excess nickel sulfide phases has been complicated by the small compositional differences between proposed phases, lack of single-crystal products, and some confusion in reporting. In their detailed review of the binary system Ni–S, Kullerud & Yund (1962) noted that the many phases which had been reported in the composition interval 30 to 33 wt.% S included: Ni_6S_5 (Schenck & Forst 1939, Lundqvist 1947, Rosenqvist 1954, Sokolova 1956), Ni_7S_6 (Peyronel & Pacilli 1942, Lundqvist 1947, Rosenqvist 1954), and Ni_9S_8 (Sokolova 1956). The experiments of Kullerud & Yund (1962) suggested the existence of two stable phases with 7:6 (metal:sulfur) stoichiometry (α-Ni_7S_6 and β-Ni_7S_6) and discredited the proposed phases with 6:5 and 9:8 stoichiometry. Kullerud & Yund reported that the low-temperature phase β-Ni_7S_6 transforms to α-Ni_7S_6 at 397°C in the presence of excess Ni_3S_2, and at 400°C with excess α-NiS. Because the present paper argues that the low-temperature phase does not have ideal 7:6 stoichiometry, this phase will be referred to as "β-Ni_7S_6", low-temperature Ni-excess nickel sulfide, or Ni_9S_8. The alpha designation for the high-temperature phase will be retained to avoid further confusion.

Lundqvist (1947) reported that the high-temperature phase has orthorhombic symmetry (*a* 11.22, *b* 16.56, *c* 3.27 Å). Fleet (1972) confirmed the orthorhombic symmetry [*a* 3.274(1), *b* 16.157(7), *c* 11.359(4) Å, *Bmmb*] and determined the crystal structure. Surprisingly, the structure of α-Ni_7S_6 has an *ideal* 6:5 stoichiometry, the 7:6 stoichiometry being accommodated by partial occupancy of the Ni positions. Three of the Ni positions are disordered, but a tendency for ordering was indicated by weak reflections of a superstructure. This was confirmed by the existence of various superstructures: 2*a*, 2*b*, 2*c*; 2*a*, 2*b*, 3*c*; and 2*a*, 2*b*, 4*c* (Putnis 1976), and 2*a*, 2*b*, 2*c* (Parise & Moore 1981).

Neither Lundqvist (1947) nor Kullerud & Yund (1962) were able to index the powder pattern of the low-temperature Ni-excess nickel sulfide phase. Lundqvist (1947) noted that the possibility of a degenerate pentlandite structure (with ideal Ni_9S_8 stoichiometry) could not be excluded. Further progress was made with the discovery of godlevskite in the Noril'sk and Talnakh Cu–Ni sulfide deposits in northern Siberia by Kulagov *et al.* (1969). These authors showed that godlevskite is a Ni-excess nickel sulfide with an orthorhombic space group (*C*222, *Cmm*2, *Amm*2, or *Cmmm*) and an X-ray powder pattern similar to that reported by Kullerud & Yund (1962) for low-temperature Ni-excess nickel sulfide.

Table 1. COMPOSITION OF GODLEVSKITE FROM NORIL'SK AND TEXMONT COMPARED WITH IDEAL (Ni_9S_8) COMPOSITION AND Ni_7S_6

	godlevskite[1] 1	2	3	Ni_9S_8	Ni_7S_6
			(wt. %)		
Fe	2.08(07)	3.0	3.65	-	-
Ni	64.45(48)	61.5	63.56	67.32	68.11
Co	0.19(02)	0.6	0.07	-	-
S	32.85(21)	35.0	32.24	32.68	31.89
	99.57	100.1	99.52	100.00	100.00
			(at. %)		
Fe	1.72	2.4	3.03	-	-
Ni	50.76	47.6	50.25	52.94	53.85
Co	0.15	0.5	0.06	-	-
S	47.37	49.6	46.67	47.06	46.15
	100.00	100.1	100.01	100.00	100.00
metal/ sulfur	1.111	1.018	1.143	1.125	1.167

[1] 1, Noril'sk, present. 2, Noril'sk, Kulagov et al. (1969). 3, Texmont, Naldrett et al. (1972).

The low Fe content of godlevskite (Table 1) is consistent with the limited solid solution of Fe in the synthetic phase (Misra & Fleet 1973). Almost immediately after the Kulagov *et al.* study, Naldrett *et al.* (1972) reported godlevskite from the Texmont mine, Ontario. Their systematic study reaffirmed the conclusion of Kulagov *et al.* (1969) concerning the equivalence of godlevskite and low-temperature Ni-excess nickel sulfide. Following the experimental work of Kullerud & Yund (1962), both of these groups of investigators assumed the ideal stoichiometry of godlevskite to be 7:6, even though the mean composition derived from the electron-microprobe data of Kulagov *et al.* indicated a stoichiometry closer to 1:1. Very recently, and after some 17 years of intermittent study of low-temperature Ni-excess nickel sulfide and godlevskite, Fleet (1987) determined the crystal structure of godlevskite and established the ideal stoichiometry as Ni_9S_8. There has been renewed interest in the thermodynamic properties and phase relations of the system Ni–S in recent years (*e.g.*, Lin *et al.* 1978, Sharma & Chang 1980, Cemic & Kleppa 1986), but these investigations have no bearing on the present study.

In the present paper, new compositional data for godlevskite and low-temperature Ni-excess nickel sulfide indicate that the true composition of both phases is Ni_9S_8. New X-ray powder data for the synthetic phase establish its true equivalence to godlevskite, and various crystal-chemical and crystallographic aspects are discussed.

GODLEVSKITE

Petrographic aspects, twinning, powder pattern and chemical composition

In the Noril'sk and Talnakh deposits, godlevskite occurs in bornite mineralization accompanying veins and massive accumulations of chalcopyrite (Kulagov *et al.* 1969). The host rocks are andesites and basalts, gabbro-dolerites and sandstones. Associated nickel sulfide minerals include millerite and pentlandite. In polished section, the godlevskite from Noril'sk and Talnakh is characterized by aggregates of twinned grains that form "elbow"-bend outlines.

In the Texmont mine, godlevskite occurs in close association with pentlandite, heazlewoodite and millerite, these forming irregular blebs of sulfide in serpentinized peridotite (Naldrett *et al.* 1972). Twinning (polysynthetic) has been observed but it is not a common feature.

The present observations were made on two samples from Noril'sk, obtained from A.E. Kulagov along with brief descriptions. In the first sample, which was the most extensively studied, godlevskite occurs with bornite, millerite, pentlandite and "nickel leaf pentlandite" (pers. comm., 1972). In the second sample, a small amount of godlevskite occurs with bornite. The study of this sample was limited to a few grain fragments removed for X-ray precession study. In the first sample, a small rock chip with a maximum diameter of 2 cm, godlevskite accounts for about 10 vol.% of all sulfides. It occurs in a matrix of chalcopyrite, as large twinned grains up to 0.4 mm in diameter (Fig. 1a), and as fine disseminations. Godlevskite is readily distinguished by its characteristic twinning, reflection pleochroism, and anisotropic colors. The reflection pleochroism is the same as described by Naldrett *et al.* (1972), pale cream to pinkish cream. Bornite is intimately intergrown with the aggregates of larger grains and forms a discontinuous rim against the chalcopyrite matrix (Fig. 1a). Individual laths of godlevskite are incipiently to completely replaced by millerite, as described by Kulagov *et al.* (1969).

As observed in polished section, twinned aggregates of godlevskite consist of either two lath-like individuals joined by a single composition plane forming an "elbow", as described by Kulagov *et al.* (1969), or as several individuals arranged in a cross or butterfly outline. All grains examined by X-ray precession are twinned on a coarse scale consistent with the texture observed in polished section. The twin operation places c^* into near coincidence with a^* (004 of the twinned crystal coincides with 400 of the untwinned crystal, *etc.*; *cf.* Table 2). Where both twin individuals are present in equal proportions, single-crystal diffraction patterns have a pseudo-tetragonal appearance (*cf.* Table 3). However, twinning is readily detected by the presence of extra reflections at extinction positions for the *C*-centered lattice. Because of the near-equality of *a* and *c* (and a^* and c^*) and the *C*222 space group, it was not possible to distinguish between the twin laws possible, using the precession photographs alone. Several twinned grains were removed from a polished section, and their orientation determined by X-ray precession. Careful study showed that the lath-like individuals (Fig. 1a) are elongate parallel to the *a* axis, and the twin composition plane is (101). Therefore, the twin axis is normal to (101). This twin law for godlevskite is different from that relevant to polysynthetic twinning in low-temperature Ni-excess nickel sulfide when transformed from α-Ni_7S_6, for which the twin axis is normal to (011) (Putnis 1976).

The X-ray powder-diffraction data of Kulagov *et al.* (1969, Table 4) have been reindexed using powder-pattern data calculated with POWDR2 (D.K. Smith, Pennsylvania State University) and the crystal-structure data of Fleet (1987): powder lines were indexed on the basis of both position and intensity. The refined unit-cell parameters (Table 3) are in good agreement with the single-crystal data of Fleet (1987).

An electron-microprobe analysis of godlevskite from Noril'sk was carried out with the JEOL JXA-8600 Superprobe at the University of Western Ontario, using synthetic NiS and FeS and metallic Co as standards. The mean data for 10 spot analyses are given in Table 1 (column 1), and are compared with the earlier data of Kulagov *et al.* (1969) and Naldrett *et al.* (1972) for godlevskite from Texmont, and the Ni_9S_8 and Ni_7S_6 compositions. The present data are consistent with 9:8 stoichiometry and certainly exclude 7:6 stoichiometry.

Table 2. POWDER DIFFRACTION DATA FOR LOW-TEMPERATURE Ni_7S_6 COMPOSITION AND GODLEVSKITE FROM NORIL'SK

Ni_7S_6[1]				heazlewoodite[2]		godlevskite[3]				
d(Å)	I	hkl	I_{calc}	d(Å)	I	d(Å)	I	d(Å)	hkl	I
7.159	-	110	7					1.608	063	10
5.708	24	111	21			5.75	20	1.576	353	10
4.706	9	002	6			4.70	10	1.521	-	10
4.664	6	200	5					1.478	533	20
4.177	17	201	18			4.14	20	1.439	354	20
4.082	16			4.081	16			1.426	622	10
3.868	15	112	12			3.93	10	1.399	080	10
-	4	022	5			3.62	20	1.363	372	10
-	5	220	5					1.349	641	10
3.311	4	202	5					1.326	463	10
3.261	49	131	58			3.28	50	1.296	373,207	10
2.998	5	310	5					1.264	-	10
2.875	76	113	56	2.8734	23	2.85	100	1.247	643,731	10
2.855	100	311,222	100					1.226	554	10
2.797	16	132	20			2.80	20	1.176	008	20
2.740	20	023	18			2.75	20	1.168	800	20
2.603	14	203	17			2.62	10	1.156	465	20
2.526	4	312	7			2.50	10	1.119	0,10,0	10
2.379	8	330	4	2.3781	8	2.40	10	1.095	194	10
2.353	9	004	8	2.3493	3	2.37	10	1.086	393	20
2.332	25	241,400	25			2.33	40	1.070	484	10
-		114				2.24	10	1.061	2,10,2	20
2.185	21	150	25			2.18	40	1.055	408	10
-		332	9			2.12	10	1.046	804	10
2.100	30	421	31			2.10	50	1.034	158	10
2.040	11			2.0404	9			1.005	4,10,1	10
1.9810	5	152	1					0.991	931	10
1.9486	5	134	7			1.941	20	0.9853	448	10
1.9102	14	243	17			1.906	30	0.9803	913	40
1.9017	11	333	13					0.9795	844	20
1.8374	21	510	4					0.9746	825	20
1.8321	19	061	18	1.8323	12	1.832	30			
1.8039	66	044,511	61	1.8186	10	1.803	90			
1.7941	77	440,025, 153	77			1.795	80			
-	6			1.6789	4	1.714	10			
1.6635	10	530	4	1.6638	14					
1.6560	75	404,135	64			1.654	80			
1.6301	22	262	19			1.625	30			

[1] interpreted to be a mixture of Ni_9S_8 and Ni_3S_2.
[2] PDS 30-863, intensities normalized to 16 for 101.
[3] Kulagov et al. (1969, Table 4), reindexed.

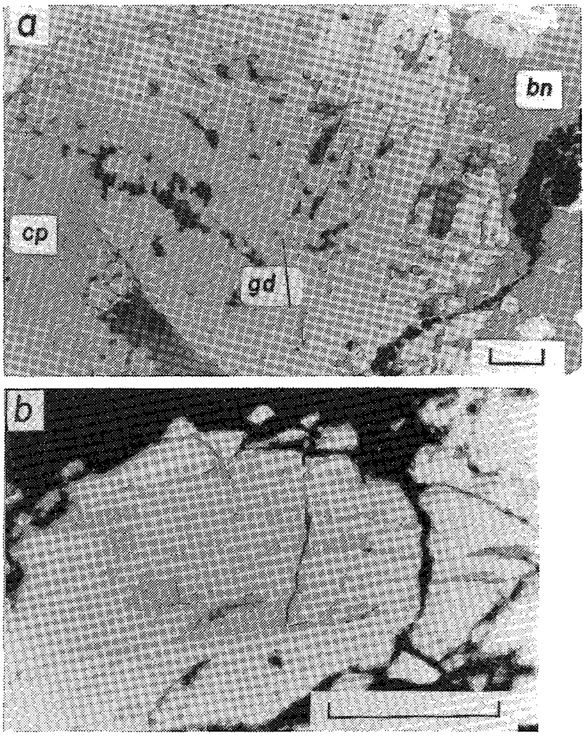

FIG. 1. Photomicrographs of: a) godlevskite (gd) from Noril'sk, intergrown with bornite (bn) in a matrix of chalcopyrite (cp); twin boundary marked by line. (b) Tarnished Ni_3S_2 lamellae in Ni_9S_8 matrix; Ni_7S_6 bulk composition; black is epoxy. Reflected light; scale bar is 0.05 mm.

Recognizing now that both the crystal structure of godlevskite and the reanalysis of godlevskite from northern Siberia indicate a 9:8 stoichiometry (and not 7:6), it is appropriate to reinterpret the analytical data of Naldrett *et al.* (1972, Table 2). The reported value of the metal/sulfur ratio for godlevskite from Texmont is intermediate between those for 9:8 and 7:6 stoichiometries. Furthermore, the compositions for the two other binary nickel sulfide phases from Texmont (heazlewoodite and millerite) are slightly metal-rich compared to their ideal stoichiometries (3:1.97 *versus* 3:2 and 1:0.99 *versus* 1:1, respectively). Applying the discrepancy for the reported heazlewoodite composition as a linear calibration correction to the godlevskite data gives an apparent minimum metal/sulfur ratio for godlevskite from Texmont of 1.127, which is close to the ideal value for 9:8 stoichiometry (Table 1). Thus there is reason to suspect that the analytical data of Naldrett *et al.* (1972) for godlevskite from Texmont may not indicate a significant departure from the ideal 9:8 stoichiometry.

It is fully appreciated that the accuracy of electron-microprobe analyses is predicated on meaningful calibration. The standard NiS and FeS of the present study were prepared under exacting laboratory con-

Table 3. UNIT-CELL PARAMETERS (Å) FOR GODLEVSKITE FROM NORIL'SK AND SYNTHETIC Ni$_9$S$_8$.

	a	b	c	
godlevskite	9.3359(7)	11.2185(10)	9.4300(6)	single crystal[1]
"	9.328(6)	11.209(7)	9.429(6)	powder[2]
"	9.18	11.29	9.47	powder[3]
Ni$_9$S$_8$	9.306(6)	11.222(7)	9.415(6)	powder[2]
"	9.327(3)	11.230(4)	9.365(3)	single crystal[4]

[1] Fleet (1987). [2] Table 1. [3] indexed by Kulagov et al. (1969). [4] twinned single crystal.

ditions and have been used for several years as standards for microprobe analysis of sulfides. The present analysis (Table 1) is not significantly different from the composition for ideal M_9S_8 stoichiometry, but it is significantly lower in metal contents than the composition for ideal M_7S_6 stoichiometry. Reanalysis in other laboratories using different standards (which accurately reproduce standard NiS and Ni_3S_2 compositions) is not expected to alter this conclusion.

Crystal structure

The crystal structure of godlevskite [$(Ni_{8.7}Fe_{0.3})S_8$, $C222$, $Z = 4$, $D_x = 5.273$ g. cm^{-3}] is based on a distorted cubic close-packed array of 32 S atoms per unit cell, with 20 Ni atoms in tetrahedral coordination and 16 in square-pyramidal coordination (Fig. 2). There are six independent tetrahedral Ni positions [Ni(1), Ni(2), Ni(3), Ni(4), Ni(5), Ni(6)], two independent square-pyramidal Ni positions

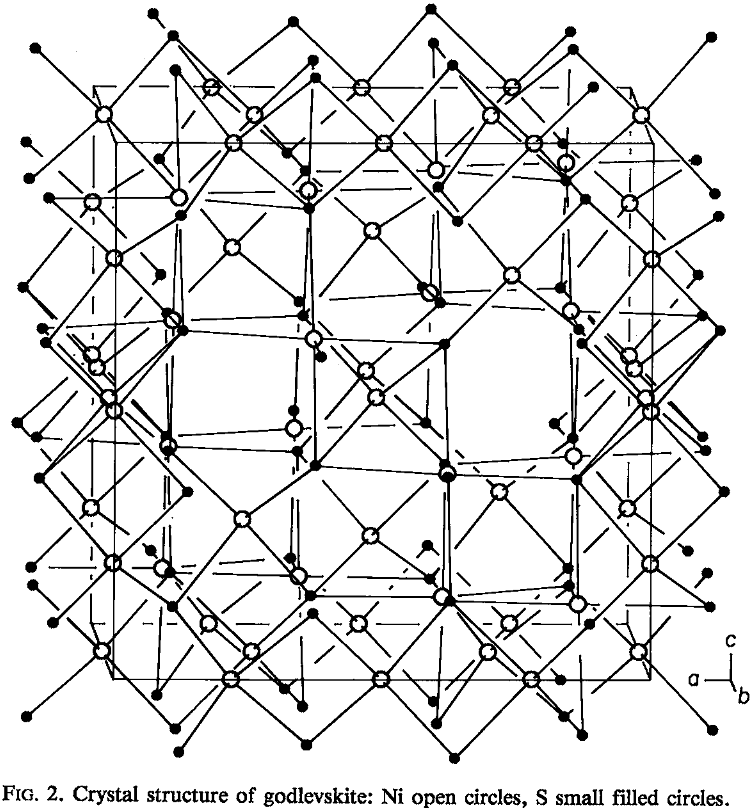

FIG. 2. Crystal structure of godlevskite: Ni open circles, S small filled circles.

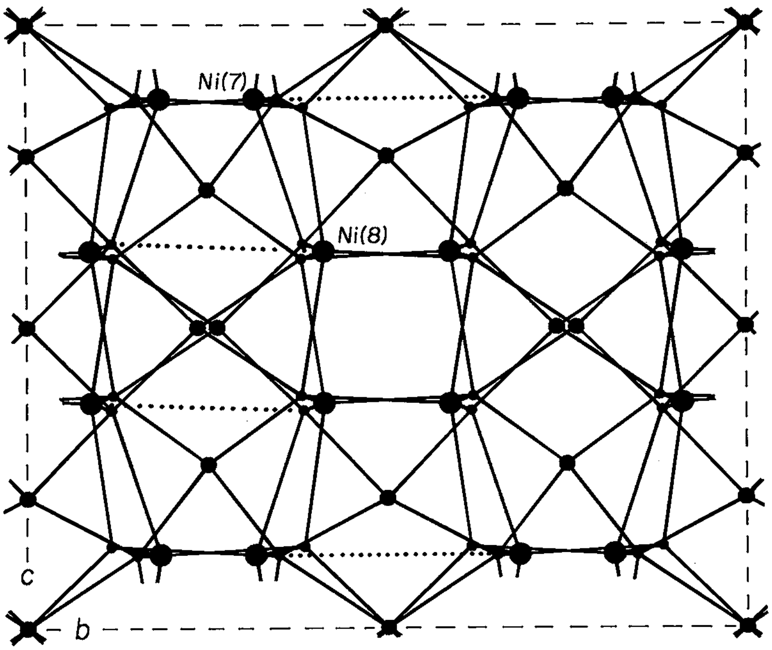

FIG. 3. Crystal structure of godlevskite in [100] projection, showing distortion by stretching parallel to [010] and development of square-pyramidal coordination from octahedral coordination of ideal structure. Ni in square pyramidal coordination, large circles; Ni in tetrahedal coordination, medium circles; S small circles; remote "sixth" S atoms, which complete NiS_6 octahedra, are located by stippled lines from selected Ni (7) and Ni (8) atoms.

[Ni(7), Ni(8)] and four independent S positions. Completion of the crystal structure analysis (Fleet 1987) was frustrated for some time by the high pseudosymmetry, structural complexity, and compositional ambiguity. The combination of pseudosymmetry and structural complexity even limits the possibilities for diagrammatic representation. However, the ideal crystal structure does afford a useful model for developing the structural details. It is based on a cubic close-packed array of sulfur atoms, 32 per unit cell, as in pentlandite [$(Fe,Ni)_9S_8$], with Ni atoms in 20 of the 64 possible tetrahedral positions and 16 of the 32 possible *octahedral* positions. Distortion of this ideal structure (principally, stretching parallel to [010], Fig. 3, and contraction normal to [010]) modifies the NiS_6 octahedra to NiS_5 square pyramids. The NiS_4 tetrahedra are associated into three-membered chains *via* shared coordination edges (Fig. 4), yielding short Ni-Ni distances. Chains of $Ni(1)S_4$-$Ni(2)S_4$, $Ni(3)S_4$-$Ni(6)S_4$ and $Ni(5)S_4$-$Ni(6)S_4$ tetrahedra are parallel to, respectively, [100], [001] and [010] (Fig. 4); the last two chains form a five-membered cross centered on Ni (6). Square-pyramids of Ni (7) S_5 and Ni (8) S_5 form both 4-fold clusters and [101] chains (Figs. 2,

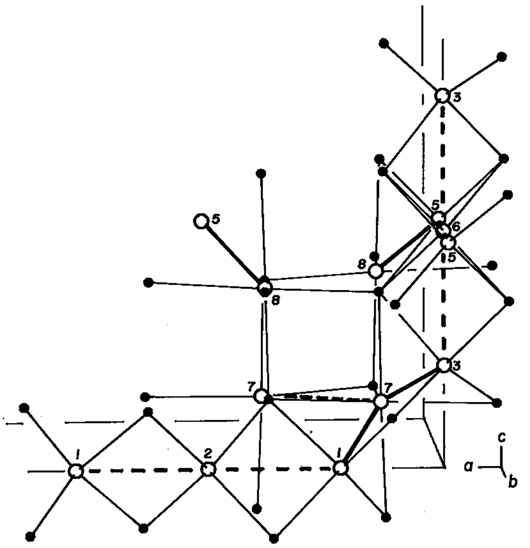

FIG. 4. Chains and crosses of NiS_4 tetrahedra, 4-fold clusters of NiS_5 square pyramids, and short Ni-Ni distances in structure of godlevskite, *cf.* Figure 2. Ni open circles; S small filled circles; heavy lines, Ni-Ni < 2.60 Å; broken heavy lines, Ni-Ni $= 2.60$–2.75 Å.

4) by sharing pyramidal and basal edges, but most of the resulting Ni–Ni interactions are longer than 2.9 Å. The shortest Ni–Ni distances project through the bases of the square pyramids (Fig. 4). These arise because the NiS_6 octahedra, formed by adding the sixth, more remote S atom to the NiS_5 square pyramids, share faces with NiS_4 tetrahedra.

LOW-TEMPERATURE NI-EXCESS NICKEL SULFIDE (Ni_9S_8)

Low-temperature Ni-excess nickel sulfide was synthesized in 1969 and 1970, when it was assumed to have ideal 7:6 stoichiometry. The starting material was the product α-Ni_7S_6 used in the study of Fleet (1972). This had been prepared by reacting Ni sponge (reduced with hydrogen at 900°C) and S crystals in an evacuated sealed silica-glass tube at 504°C for 9 days. The crushed product α-Ni_7S_6 was annealed in a sealed silica-glass tube at 297°C for 49 days.

Examination, at the time of synthesis, by polished section and X-ray powder and single-crystal diffraction procedures, suggested that the annealed product was the homogeneous β-Ni_7S_6 phase of Kullerud & Yund (1962). The powder pattern (Table 2) was equivalent to that of Kullerud & Yund (1962, Table 18) but remained unindexed. Grain fragments were twinned and gave pseudo-tetragonal unit-cell parameters (Table 3). An attempt at structure analysis was unsuccessful. Several subsequent attempts at structure analysis with fragments of twinned grains from Noril'sk also were unsuccessful. However, the intensity and unit-cell data obtained from the natural material permitted the *original* powder pattern of the Ni_7S_6 bulk composition to be indexed. A TEM analysis confirmed that the diffraction pattern of low-temperature Ni-excess nickel sulfide was consistent with space groups *C*222, *Cmm*2, *Cmmm*, and possibly *C*222$_1$, and that no other diffraction effects (consistent with domain structure, *etc.*) are present. The structural information gleaned at this time (1983) indicated a pentlandite-like (9:8) stoichiometry for both godlevskite and synthetic low-temperature Ni-excess nickel sulfide. On further examination, this was supported by the presence of excess heazlewoodite (Ni_3S_2) in the annealed Ni_7S_6 bulk composition, as indicated by heazlewoodite lines in the indexed powder pattern (Table 2), heazlewoodite reflections on precession films, and heazlewoodite exsolution in the tarnished polished section.

The *original* powder pattern was obtained with a Jagodzinski focusing powder camera and was calibrated with α-quartz (Fleet 1968) (Table 2). The intensity data were obtained recently by planimetry from a single Joyce-Loebl densitometer scan magnified by an electrostatic copier. These data, when corrected for interference by heazlewoodite lines, are in remarkably good agreement with intensities calculated by POWDR2 using the structural data for godlevskite (Fleet 1987) (Table 2). Refined unit-cell parameters for the indexed powder pattern are in better agreement with the unit-cell parameters for godlevskite than the data for the twinned single crystal (Table 2). Small remaining discrepancies with the single-crystal data for godlevskite may be attributable to the small extent of Fe substitution in the natural material (Table 1), which would be expected to result in a decrease in unit-cell volume. The heazlewoodite 110 line accounts for 26% of the intensity of the 2.875 Å line of the powder pattern for the bulk Ni_7S_6 composition. The proportion of heazlewoodite present, estimated semi-quantitatively from the sums of the calculated intensities for godlevskite and of the normalized intensities for heazlewoodite, gave 13.2% (by diffraction volume).

In polished surfaces exposed to air, heazlewoodite develops a much stronger tarnish than low-temperature Ni-excess nickel sulfide (Fig. 1b). The apparent proportion of heazlewoodite in the annealed Ni_7S_6 bulk composition, as observed in tarnished polished section, varies up to a maximum of about 25%. This appears to indicate that the exsolved heazlewoodite is present as flame- or ribbon-like lamellae. The weak heazlewoodite reflections in precession films were randomly oriented. The heazlewoodite lamellae are, therefore, incoherent with the matrix of low-temperature Ni-excess nickel sulfide.

DISCUSSION

Structure and composition of low-temperature Ni-excess nickel sulfide

The good agreement between the observed intensities of powder diffraction lines for low-temperature Ni-excess nickel sulfide and the calculated intensities for godlevskite (Table 2) is final confirmation of the equivalence of the synthetic and natural phases (Kulagov *et al.* 1969, Naldrett *et al.* 1972). Low-temperature Ni-excess nickel sulfide clearly has the crystal structure of godlevskite (Fleet 1987) with ideal 9:8 stoichiometry. Its formal composition is Ni_9S_8.

The present analytical data and the structure analysis of Fleet (1987) both indicate that the composition of godlevskite is very close (virtually identical) to the ideal 9:8 stoichiometry. On the other hand, both synthetic and natural pentlandite, $(Fe,Ni)_9S_8$, exhibit deviation from ideal 9:8 stoichiometry and are commonly slightly metal-rich (Knop *et al.* 1965, Harris & Nickel 1972, Misra & Fleet 1973). Theoretically, synthetic Ni_9S_8 could have a composition of either $Ni_{9+x}S_8$ or Ni_9S_{1-x}. However, the present experimental data suggest that, like godlevskite, equilibrated synthetic Ni_9S_8 has a composition close to the ideal 9:8 stoichiometry. On annealing at

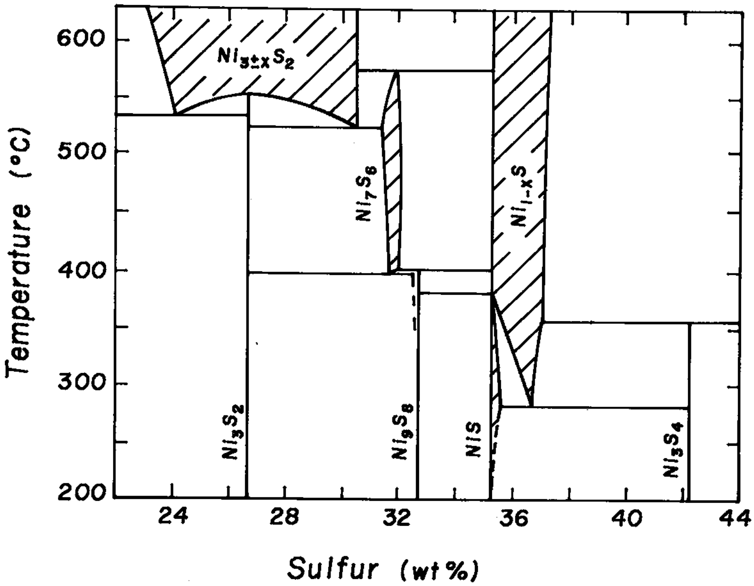

FIG. 5. Schematic revision of the low-temperature phase relations of the system Ni–S (Kullerud & Yund 1962, Fig. 2), showing the proposed composition line of low-temperature Ni-excess nickel sulfide (Ni_9S_8). The extent of solid solution above 300°C is uncertain.

297°C, α-Ni_7S_6 disproportionates to (Ni_9S_8 + Ni_3S_2) according to the reaction: 3α-$Ni_7S_6 = 2Ni_9S_8 + Ni_3S_2$. The proportion of heazlewoodite estimated from the powder-diffraction pattern (13.2%) is in very good agreement with the proportion of exsolved heazlewoodite in the annealed Ni_7S_6 composition calculated according to this reaction (13.3 wt.%). This agreement is further supported by the porportion of heazlewoodite observed in tarnished polished section.

The present conclusion on the range in composition of synthetic Ni_9S_8 is at variance with the experimental work of Kullerud & Yund (1962). However, the heazlewoodite 101 (4.081 Å) and 202 (2.0404 Å) lines are visible in the powder-diffraction pattern of the low-temperature Ni_7S_6 composition published by Kullerud & Yund (1962, Fig. 6), although the apparent proportion of heazlewoodite is less than that observed in the present study.

The low-temperature phase relations of the system Ni–S as depicted in Figure 2 of Kullerud & Yund (1962) have been revised to include the proposed Ni_9S_8 stoichiometry of low-temperature Ni-excess nickel sulfide (Fig. 5). Phase relations for the proposed Ni_4S_3 phase of Lin *et al.* (1978) and Sharma & Chang (1980), which would replace the $Ni_{3-x}S_2$ composition field, have not been included. The present study has not investigated the possibility of a stable solid-solution field for compositions more Ni-rich than Ni_9S_8 above 300°C, the existence of which would explain partly the discrepancies with Kullerud & Yund (1962).

Twinning and crystal structure

The present study has shown that the characteristic elbow-like twins of godlevskite from Noril'sk and Talnakh have a (101) composition plane and twin law with twin axis normal to (101). This twin law seems to follow directly from the pseudo-tetragonal symmetry of the unit-cell (Table 3) and the high pseudosymmetry of the crystal structure (Fig. 2). A (101) composition plane that includes the Ni(4), Ni(5), Ni(7) and Ni(8) positions (Fig. 2), for example, would yield a twin structure that preserves the integrity of the square-pyramidal and tetrahedral coordination polyhedra. The twin law with twin axis normal to (011), for polysynthetic twinning in synthetic Ni_9S_8 transformed from α-Ni_7S_6 (Putnis 1976), must result in a more complicated twin structure (Fig. 3). It is presumably reaction-path dependent, and a rationalization for it does not seem possible in the absence of an orientation relationship with the precursor α-Ni_7S_6 phase.

Comparison with other sulfide structures

The crystal structure of godlevskite is very much a hybrid of the structural elements of several related phases (pentlandite, millerite and α-Ni_7S_6). Although there are similarities in the unit cells, powder patterns, and arrays of S atoms of godlevskite and pentlandite, godlevskite does not have a pentlandite-derivative crystal structure. In the crystal structure of pentlandite (*e.g.*, Hall & Stewart 1973), 32 metal (*M*) atoms per unit cell are in tetrahedral coordination with sulfur, and only 4 are in octahedral coordination. Short *M–M* distances arise through shared tetrahedral edges, the MS_4 tetrahedra being associated into "cubic" clusters. In millerite (Grice & Ferguson 1974, Rajamani & Prewitt 1974), Ni is 5-fold coordinated within an approximately square-pyramidal polyhedron of S atoms (the apical S is offset from the pyramid axis). The NiS_5 square pyramids are associated into 3-fold clusters through the sharing of basal edges, which results in two short Ni–Ni bonds per Ni atom (*e.g.*, Fig. 2 of Fleet 1972). In the crystal structure of α-Ni_7S_6 (Fleet 1972), four of the Ni positions are in square-pyramidal coordination with S, and one is in tetrahedral coordination. Short Ni–Ni distances arise through shared coordination edges; the 3-fold clusters of the Ni(2)S_5 and Ni(5)S_5 square pyramids (Fig. 1 of Fleet 1972) are equivalent to the 3-fold clusters of NiS_5 polyhedra in millerite. In the crystal structure of heazlewoodite (Ni_3S_2, Fleet 1977, Parise 1980), each Ni atom is coordinated to four S atoms, forming a NiS_4 tetrahedron, and to four other Ni atoms, through the sharing of edges of NiS_4 tetrahedra.

In summary, the structure of godlevskite has fewer tetrahedrally coordinated Ni atoms than pentlandite, and fewer Ni atoms in square-pyramidal coordination than either millerite or α-Ni_7S_6. Short Ni–Ni distances arise both from shared NiS_4 coordination edges, as in pentlandite, and through the bases of NiS_5 square pyramids, as in millerite and α-Ni_7S_6. Three-fold clusters of short (and presumably bonded) Ni–Ni distances (Ni_3 clusters), proposed as a stabilizing unit in metal-bonded nickel sulfides (Parise & Moore 1981) and present in millerite, α-Ni_7S_6 and heazlewoodite, are not present in godlevskite.

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REFERENCES

FLEET, M.E. (1968): On the lattice parameters and superstructures of pyrrhotites. *Amer. Mineral.* **53**, 1846-1855.

_____ (1972): The crystal structure of α-Ni_7S_6. *Acta Cryst.* **B28**, 1237-1241.

_____ (1977): The crystal structure of heazlewoodite, and metallic bonds in sulfide minerals. *Amer. Mineral.* **62**, 341-345.

_____ (1987): Structure of godlevskite, Ni_9S_8. *Acta Cryst.* **C43**, 2255-2257.

CEMIC, L. & KLEPPA, O.J. (1986): High temperature calorimetry of sulfide systems. I. Thermochemistry of liquid and solid phases of Ni + S. *Geochim. Cosmochim. Acta* **50**, 1633-1641.

GRICE, J.D. & FERGUSON, R.B. (1974): Crystal structure refinement of millerite (β-NiS). *Can. Mineral.* **12**, 248-252.

HALL, S.R. & STEWART, J.M. (1973): The crystal structure of argentian pentlandite $(Fe,Ni)_8AgS_8$, compared with the refined structure of pentlandite $(Fe,Ni)_9S_8$. *Can. Mineral.* **12**, 169-177.

HARRIS, D.C. & NICKEL, E.H. (1972): Pentlandite compositions and associations in some mineral deposits. *Can. Mineral.* **11**, 861-878.

KNOP, O., IBRAHIM, M.A. & SUTARNO (1965): Chalcogenides of the transition elements. IV. Pentlandite, a natural π phase. *Can. Mineral.* **8**, 291-316.

KULAGOV, E.A., EVSTIGNEEVA, T.L. & YUSHKO-ZAKHAROVA, O.E. (1969): The new nickel sulfide, godlevskite. *Geol. Rudnykh. Mestorozhderii* **11**, 115-121. (In Russ.).

KULLERUD, G. & YUND, R.A. (1962): The Ni–S system and related minerals. *J. Petrology* **3**, 126-175.

LIN, R.Y., HU, D.C. & CHUNG, Y.A. (1978): Thermodynamics and phase relations of transition metal–sulfur systems. II. The nickel–sulfur system. *Metallurgical Trans.* **9B**, 531-538.

LUNDQVIST, D. (1947): X-ray studies on the binary system Ni–S. *Arkiv. Kemi, Mineral. Geol.* **24A**, no. 21, 1-12.

MISRA, K.C. & FLEET, M.E. (1973): The chemical compositions of synthetic and natural pentlandite assemblages. *Econ. Geol.* **68**, 518-539.

NALDRETT, A.J., GASPARRINI, E., BUCHAN, R. & MUIR, J.E. (1972): Godlevskite (β-Ni_7S_6) from the Texmont mine, Ontario. *Can. Mineral.* **11**, 879-885.

PARISE, J.B. (1980): Structure of heazlewoodite (Ni_3S_2). *Acta Cryst.* **B36**, 1179-1180.

_____ & MOORE, F.H. (1981): A superstructure of α-Ni_7S_6 and its relationship to heazlewoodite (Ni_3S_2) and millerite (NiS). *Twelfth Int. Conf. Crystallography, Collected Abstr.* **C-182**.

PEYRONEL, G. & PACILLI, E. (1942): Contributo alla conoscenza del sistema Nichelio-Zolfo. *Atti R. Accad. Italia, Rend. classe sci.fis.-mat.* (7) **3**, 278-288.

PUTNIS, A. (1976): Observations of transformation behavior in Ni_7S_6 by transmission electron microscopy. *Amer. Mineral.* **61**, 322-325.

RAJAMANI, V. & PREWITT, C.T. (1974): The crystal structure of millerite. *Can. Mineral.* **12**, 253-257.

ROSENQVIST, T. (1954): A thermodynamic study of the iron, cobalt, and nickel sulphides. *J. Iron Steel Inst.* **176**, 37-57.

SCHENCK, R. & FORST, P. VON DER (1939): Gleichgewichtsstudien an erzbildenden Sulfiden II. *Z. anorg. Chem.* **241**, 145-157.

SHARMA, R.C. & CHANG, Y.A. (1980): Thermodynamics and phase relationships of transition metal–sulfur systems: IV. Thermodynamic properties of the Ni–S liquid phase and the calculation of the Ni–S phase diagram. *Metallurgical Trans.* **11B**, 139-146.

SOKOLOVA, M.A. (1956): Investigation of the nickel–sulfur system having 30–50 atomic percent sulfur. *Dokl. Akad. Nauk SSSR.* **106**, 286-289. (In Russ.).

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