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Structure of Godlevskite, Ni_9S_8

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Abstract. $(Ni_{8.7}Fe_{0.3})S_8$, $M_r = 784{\cdot}1$, orthorhombic, $C222$, $a = 9{\cdot}3359\ (7)$, $b = 11{\cdot}2185\ (10)$, $c = 9{\cdot}4300\ (6)$ Å, $V = 987{\cdot}7$ Å^3, $Z = 4$, $D_x = 5{\cdot}273$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 180{\cdot}06$ cm^{-1}, $F(000) = 1518$, room temperature, final $R = 0{\cdot}041$ for 1743 unique reflections. The crystal structure of godlevskite 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. The ideal stoichiometry is established as Ni_9S_8. NiS_4 tetrahedra form clusters of three-membered chains and five-membered crosses, and NiS_5 square pyramids form fourfold clusters and chains. The structure contains elements of the structures of the related phases α-Ni_7S_6, millerite (NiS) and pentlandite $[(Fe,Ni)_9S_8]$.

Introduction. Godlevskite (Ni_9S_8) was originally described from the Noril'sk and Talnakh Cu–Ni sulfide deposits in northern Siberia (Kulagov, Evstigneeva & Yushko-Zakharova, 1969), and was subsequently reported in a nickel sulfide ore from the Texmont mine, Ontario (Naldrett, Gasparrini, Buchan & Muir, 1972). Both of these studies recognized godlevskite as a metal-excess nickel sulfide mineral equivalent to the synthetic low-temperature Ni-excess phase previously referred to as 'β-Ni_7S_6' (*e.g.* Kullerud & Yund, 1962). Lundqvist (1947) and Kullerud & Yund (1962) did not index the powder pattern of 'β-Ni_7S_6', but Lundqvist noted that the possibility of a degenerate pentlandite structure for the phase could not be excluded. Kulagov *et al.* (1969) reported that the X-ray single-crystal and powder diffraction patterns of godlevskite were consistent with the space groups $C222$, $Cmm2$, $Amm2$, and $Cmmm$, with $a = 9{\cdot}18$, $b = 11{\cdot}29$, $c = 9{\cdot}47$ Å.

In the present study, godlevskite is shown to have a crystal structure based on a distorted cubic close-packed array of S atoms, with 20 Ni atoms per unit cell in tetrahedral coordination and 16 in square-pyramidal coordination. The ideal stoichiometry is established as Ni_9S_8. Other aspects of godlevskite and synthetic Ni_9S_8 will be discussed elsewhere (Fleet, 1988).

Experimental. The godlevskite specimen was from the Noril'sk Cu–Ni sulfide deposit. It occurs as twinned crystals enclosed by chalcopyrite ($CuFeS_2$) and intergrown with bornite (Cu_5FeS_4) and millerite (NiS) (Kulagov *et al.*, 1969). The crystal was rectangular in shape with approximate dimensions $0{\cdot}10 \times 0{\cdot}12 \times 0{\cdot}13$ mm and a calculated volume of $0{\cdot}17 \times 10^{-2}$ mm^3. It was removed from a polished thin section, and size-reduced with 600 abrasive paper. A preliminary X-ray precession study confirmed that the diffraction pattern was consistent with space groups $C222$, $Cmm2$, $Amm2$, $Cmmm$ and, possibly, $C222_1$, and revealed very weak reflections of a second phase (chalcopyrite?) and weak twin-related reflections [twin plane, (101)]. Enraf–Nonius CAD-4*F* diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 20 reflections in 2θ range 53·5–60·8° for cell parameters. Data collected by θ–2θ scan; scan angle $(2\theta) = 2{\cdot}4°$, with dispersion correction. 4387 hkl, $-hkl$ reflections permitted by space group $C222$ out to $2\theta = 90°$ measured, but structure refinement limited to data with $2\theta \leq 80°$; $-16 \leq h \leq 16$, $0 \leq k \leq 20$, $0 \leq l \leq 17$. Standard reflections 044, $04\bar{4}$, 800; $R_{\mathrm{int}} = 0{\cdot}02$, no significant decline in intensity. Background, Lorentz, polarization and absorption corrections applied; transmission factors (by Gaussian integration with a $12 \times 12 \times 12$ grid) varied from 0·136 for 020 to 0·258 for $\bar{6}$,20,5. 1743 unique reflections. 389 reflections considered unobserved $[I \leq 3\sigma(I)]$; $\sigma(I) = [I_m + 0{\cdot}002^2(I_m - B)^2 + 0{\cdot}005^2(I - I_m)^2]^{1/2}$; I_m, measured intensity and B, background. Data set corrected for interference due to 2·4% (by diffraction volume) of a twin component, following measurements on 30 strongest reflections with $(h + l) \neq 2n$.

Crystal-structure analysis was complicated by pseudosymmetry, space-group ambiguity and poor diffraction quality of both synthetic (Fleet, 1988) and

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Table 1. *Positional and equivalent isotropic thermal parameters* (Å^2) *for godlevskite* (Ni_9S_8) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	Equipoint	x	y	z	B_{eq}
Ni(1)	4(*e*)	0·22010 (10)	0·0	0·0	0·52 (3)
Ni(2)	2(*b*)	0·0	0·5	0·0	0·44 (4)
Ni(3)	4(*i*)	0·0	0·0	0·21521 (11)	0·54 (3)
Ni(4)	4(*k*)	0·25	0·25	0·27187 (13)	0·51 (3)
Ni(5)	4(*h*)	0·0	0·23652 (10)	0·5	0·76 (4)
Ni(6)	2(*d*)	0·0	0·0	0·5	0·74 (5)
Ni(7)	8(*l*)	0·37369 (10)	0·68414 (6)	0·12145 (9)	0·48 (2)
Ni(8)	8(*l*)	0·12569 (10)	0·58779 (6)	0·37368 (10)	0·51 (2)
S(1)	8(*l*)	0·13268 (15)	0·61610 (12)	0·13483 (17)	0·51 (4)
S(2)	8(*l*)	0·36724 (15)	0·61693 (12)	0·36158 (16)	0·53 (4)
S(3)	8(*l*)	0·38213 (17)	0·34835 (13)	0·11982 (18)	0·56 (4)
S(4)	8(*l*)	0·11977 (19)	0·38020 (13)	0·38590 (17)	0·60 (5)

Table 2. *Anisotropic thermal parameters* (× 10^3 Å^2) for *the refined structure of godlevskite*

Anisotropic temperature factors have the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni(1)	600 (27)	397 (34)	552 (32)	0	0	95 (32)
Ni(2)	542 (40)	479 (48)	398 (44)	0	0	0
Ni(3)	566 (27)	476 (33)	577 (31)	119 (33)	0	0
Ni(4)	511 (31)	450 (33)	576 (38)	−15 (27)	0	0
Ni(5)	1096 (33)	341 (36)	837 (36)	0	−392 (39)	0
Ni(6)	758 (48)	845 (54)	621 (46)	0	0	0
Ni(7)	497 (23)	478 (19)	473 (26)	36 (21)	−5 (23)	−21 (21)
Ni(8)	460 (24)	648 (20)	430 (24)	39 (22)	22 (23)	−73 (22)
S(1)	495 (39)	565 (35)	461 (41)	−8 (45)	17 (46)	−25 (36)
S(2)	507 (36)	701 (35)	393 (40)	30 (46)	−97 (44)	−92 (34)
S(3)	486 (43)	654 (37)	525 (44)	−130 (39)	−67 (45)	10 (39)
S(4)	632 (51)	678 (39)	502 (49)	99 (46)	42 (38)	−70 (40)

recoverable natural crystals. Direct methods and analogy with structures of related compositions [*e.g.* α-Ni_7S_6 (Fleet, 1972); maucherite ($Ni_{11}As_8$) (Fleet, 1973); millerite (NiS) (Rajamani & Prewitt, 1974; Grice & Ferguson, 1974)] yielded sufficient information to proceed with trial structures. Final structure emerged in *C*222 when Ni atoms in tetrahedral coordination were placed in special positions. $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2$; weak reflections $[|F_o| < (|F_o|_{max}/20)]$ were given a low weight ($\sigma = 1000$). Refinement using all data out to $2\theta = 80°$ and 82 variable parameters converged to $R = 0{\cdot}041$, $wR = 0{\cdot}022$, $S = 0{\cdot}079$, $(\Delta/\sigma)_{max} = 4 \times 10^{-4}$, $\Delta\rho = -7{\cdot}1$ to $7{\cdot}4$ e Å^{-3}. The low value of *S* reflects the low weight given to the weak reflections. Minimum and maximum residual electron density is associated with Ni(1) and Ni(7), respectively. There were no evident problems with the refinement, no correlation coefficients greater than 0·5 and no non-positive-definite temperature factors. The isotropic extinction parameter for type I extinction (*g*; Coppens & Hamilton, 1970) is 0·084 (2) × 10^{-4}. Scattering factors for neutral atomic species and f', f'' taken from *International Tables for X-ray Crystallography* (1974). Computations carried out with *DATAP*77 and *LINEX*77 (State University of New York at Buffalo).

Table 3. *Selected interatomic distances* (Å) *and bond angles* (°) *in godlevskite*

Ni(1)—S(1^{v})	2·281 (2)	Ni(1)—S(3^{v})	2·254 (2)
Ni(1)—Ni(2)	2·613 (1)	Ni(1)—Ni(7^{v})	2·519 (1)
Ni(2)—S(1)	2·202 (1)	Ni(3)—S(2^{iv})	2·272 (2)
Ni(3)—S(3^{iv})	2·217 (2)	Ni(3)—Ni(6)	2·686 (1)
Ni(3)—Ni(7^{iv})	2·538 (1)	Ni(4)—S(3)	2·190 (2)
Ni(4)—S(4)	2·184 (2)	Ni(5)—S(2^{iv})	2·245 (2)
Ni(5)—S(4)	2·237 (2)	Ni(5)—Ni(6)	2·653 (1)
Ni(5)—Ni(8^{i})	2·585 (1)	Ni(6)—S(2^{iv})	2·227 (1)
Ni(7)—S(1)	2·379 (2)	Ni(7)—S(1^{v})	2·245 (2)
Ni(7)—S(2)	2·387 (2)	Ni(7)—S(3^{i})	2·306 (2)
Ni(7)—S(3^{ii})	2·309 (1)	Ni(7)—S(3)	3·768 (2)
Ni(7)—Ni(7^{v})	2·742 (2)	Ni(8)—S(1)	2·276 (2)
Ni(8)—S(2)	2·282 (1)	Ni(8)—S(4)	2·332 (2)
Ni(8)—S(4^{i})	2·296 (2)	Ni(8)—S(4^{ii})	2·322 (2)
Ni(8)—S(2^{v})	3·315 (2)		
S(1^{v})—Ni(1)—S(1^{vi})	105·89 (8)	S(1^{v})—Ni(1)—S(3^{v})	114·00 (7)
S(1^{v})—Ni(1)—S(3^{vi})	95·94 (6)	S(3^{v})—Ni(1)—S(3^{vi})	129·91 (9)
S(1)—Ni(2)—S(1^{i})	111·53 (8)	S(1)—Ni(2)—S(1^{ii})	109·45 (8)
S(1)—Ni(2)—S(1^{iii})	107·46 (8)	S(3^{v})—Ni(3)—S(2^{iv})	94·26 (5)
S(3^{v})—Ni(3)—S(2^{v})	114·76 (6)	S(3^{v})—Ni(3)—S(3^{iv})	132·12 (9)
S(2^{iv})—Ni(3)—S(2^{v})	105·18 (9)	S(3^{v})—Ni(4)—S(3)	98·19 (10)
S(3^{v})—Ni(4)—S(4)	110·23 (6)	S(3^{v})—Ni(4)—S(4^{v})	107·40 (6)
S(4)—Ni(4)—S(4^{v})	121·00 (10)	S(2^{iv})—Ni(5)—S(4)	115·27 (6)
S(2^{iv})—Ni(5)—S(2^{vi})	106·60 (9)	S(2^{iv})—Ni(5)—S(4^{iii})	115·74 (6)
S(4)—Ni(5)—S(4^{iii})	87·82 (9)	S(2^{iv})—Ni(6)—S(2^{v})	108·25 (8)
S(2^{iv})—Ni(6)—S(2^{vi})	107·83 (7)	S(2^{v})—Ni(6)—S(2^{vi})	112·37 (7)
S(1)—Ni(7)—S(1^{v})	106·99 (5)	S(1)—Ni(7)—S(2)	79·89 (6)
S(1)—Ni(7)—S(3^{i})	91·94 (7)	S(1)—Ni(7)—S(3^{ii})	152·07 (6)
S(1^{v})—Ni(7)—S(2)	105·14 (6)	S(1^{v})—Ni(7)—S(3^{i})	102·37 (7)
S(1^{v})—Ni(7)—S(3^{ii})	100·61 (6)	S(2)—Ni(7)—S(3^{i})	152·49 (6)
S(2)—Ni(7)—S(3^{ii})	88·93 (6)	S(3^{i})—Ni(7)—S(3^{ii})	86·26 (8)
S(1)—Ni(8)—S(4)	100·89 (6)	S(1)—Ni(8)—S(2)	84·38 (6)
S(1)—Ni(8)—S(4^{i})	162·98 (6)	S(1)—Ni(8)—S(4^{ii})	93·20 (7)
S(4)—Ni(8)—S(2)	99·73 (7)	S(4)—Ni(8)—S(4^{i})	96·13 (6)
S(4)—Ni(8)—S(4^{ii})	97·39 (7)	S(2)—Ni(8)—S(4^{i})	92·91 (8)
S(2)—Ni(8)—S(4^{ii})	162·87 (5)	S(4^{i})—Ni(8)—S(4^{ii})	84·44 (8)

Symmetry code: (i) $x, -y, -z$; (ii) $-x, -y, z$; (iii) $-x, y, -z$; (iv) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

Discussion. Discrepancies between the present unit-cell parameters for godlevskite and the powder data of Kulagov *et al.* (1969) and Naldrett *et al.* (1972) are attributable to incorrectly indexed powder lines (Fleet, 1988). Discrepancies between the chemical composition used in the present study and the analytical data of Kulagov *et al.* (1969) and Naldrett *et al.* (1972) are attributable to advances in electron microprobe technology and calibration procedures (Fleet, 1988).

Positional parameters for godlevskite are given in Table 1, anisotropic thermal parameters in Table 2, and selected interatomic distances and bond angles in Table 3.*

The ideal crystal structure of godlevskite is based on a cubic close-packed array of S 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] and

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* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44230 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

contraction normal to [010]) modifies the NiS_6 octahedra to NiS_5 square pyramids (Figs. 1 and 2, Table 3). Thus, Ni(1), Ni(2), Ni(3), Ni(4), Ni(5) and Ni(6) are in tetrahedral coordination with S, and Ni(7) and Ni(8) are in square-pyramidal coordination. The stoichiometry of godlevskite is established, therefore, as Ni_9S_8. Metal-site-occupancy refinement and inspection of bond distances did not reveal any evidence of Ni,Fe ordering.

NiS_4 tetrahedra are associated into three-membered chains *via* shared edges (Figs. 1 and 2), 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]; the latter two chains form a five-membered cross centred on Ni(6). $Ni(7)S_5$ and $Ni(8)S_5$ square pyramids form both fourfold clusters and [101] chains (Figs. 1 and 2) 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 (Table 3, Fig. 2). These arise because the NiS_6 octahedra, formed by adding the sixth, more remote, S atom (Table 3) to the NiS_5 square pyramids, share faces with NiS_4 tetrahedra.

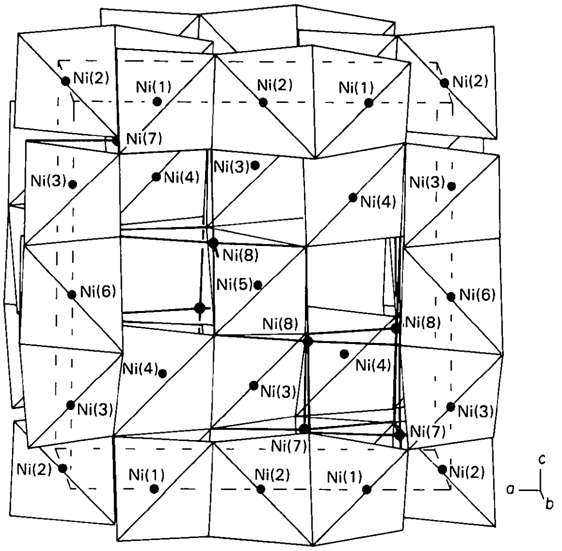

Fig. 1. Polyhedral representation of the crystal structure of godlevskite.

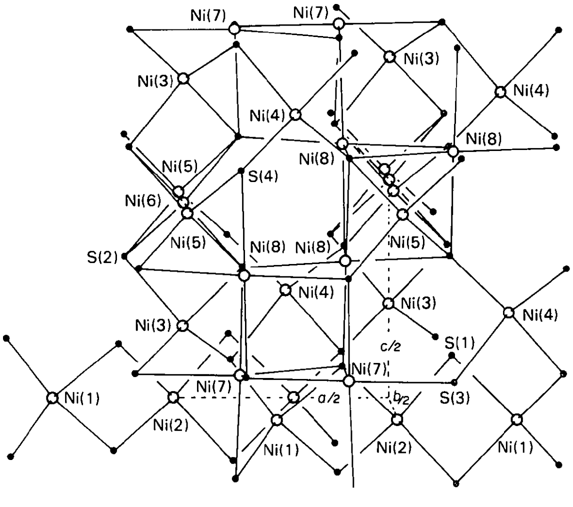

Fig. 2. Part of the crystal structure of godlevskite, showing details of the association of NiS_4 and NiS_5 coordination polyhedra: Ni, open circles; S, small filled circles.

Although there are similarities in the unit cells, powder patterns and S-atom arrays of godlevskite and pentlandite, godlevskite does not have a pentlandite-derivative crystal structure. In the structure of pentlandite (*e.g.* Hall & Stewart, 1973), 32 metal (M) atoms per unit cell are in tetrahedral coordination and four are in octahedral coordination. Short M—M distances arise only through shared tetrahedral edges, the MS_4 tetrahedra forming 'cubic' clusters. The godlevskite structure is very much a hybrid of the structural elements of several related phases (α-Ni_7S_6, millerite and pentlandite). Mean Ni—S distances (2·23 Å for NiS_4 and 2·31 Å for NiS_5) and short Ni—Ni distances (Table 3) are similar to equivalent interatomic distances in α-Ni_7S_6 (Fleet, 1972), millerite (Grice & Ferguson, 1974; Rajamani & Prewitt, 1974), and heazlewoodite (Ni_3S_2, Fleet, 1977). However, three-membered (triangular) clusters of Ni atoms with short Ni—Ni distances are not present in godlevskite; *e.g.* Ni(7)—Ni(1) = 2·52, Ni(7)—Ni(3) = 2·54 Å, but Ni(1)—Ni(3) = 2·89 Å.

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