

## Structure of Hazelwoodite (Ni<sub>3</sub>S<sub>2</sub>)

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**Abstract.** Synthetic Ni<sub>3</sub>S<sub>2</sub>, trigonal, *R*32, *a* = 4.0718 (6) Å, *α* = 89.459 (9)°, *Z* = 1, *D<sub>x</sub>* = 3.71 Mg m<sup>-3</sup>. For 130 unique intensities *R* = 0.036. Short Ni–Ni distances within and between Ni<sub>3</sub> triangles in the structure are 2.5319 (9) and 2.4966 (4) Å respectively. The two unique Ni–S distances are 2.2534 (5) and 2.2914 (5) Å.

**Introduction.** Despite qualitative confirmation (Peacock, 1947) and quantitative refinement from powder X-ray data (Fleet, 1977), some authors have questioned the correctness of the structure of hazelwoodite (Ni<sub>3</sub>S<sub>2</sub>) originally proposed by Westgren (1938). This is due to the compound's failure to agree with the predictions of the valence rules of Hulliger (1968) and Pearson (1972), which has prompted Prewitt & Rajamani (1974) and, more recently, Vaughan & Craig (1978) to suggest the structure may be incorrect.

However, because of a lack of suitable material, it has not been possible to undertake a precise study of hazelwoodite. As part of a more general study of the structural details of the phases in the Ni–S system, single crystals were grown in order to refine the structure of Ni<sub>3</sub>S<sub>2</sub>.

A stoichiometric mixture of nickel, which had previously been reduced at 873 K in a stream of hydrogen gas for 2 h, and sulphur was heated at 1033 K for 3 d in an evacuated silica-glass capsule. After quenching in iced water, the material was crushed and several small chips were separated by sieving. These were investigated by standard X-ray photographic techniques. Although many of the specimens were found to be multiple crystals, some were single and showed the expected  $\bar{3}m$  Laue symmetry and systematic extinction of reflexions consistent with the space group *R*32.

One of these fragments, a regular prism 56 × 90 × 82 μm, was chosen for data collection. It was mounted in a random orientation on the Australian Atomic Energy Commission's four-circle X-ray diffractometer. 1575 reflexions were collected with the following experimental conditions: unfiltered Mo radiation, hyper-pure *n*-type Si solid-state detector,  $\omega$ – $2\theta$  step-scan technique, 5° <  $2\theta$  < 70°.

The data were corrected for systematic variation in the X-ray-beam intensity, absorption ( $\mu = 21.2 \text{ mm}^{-1}$ ), Lorentz and polarization effects. Symmetry-related intensities were averaged. The final data set contained 130 independent reflexions. All data, including those with negative intensity, were used in the subsequent refinement.

The structural parameters given by Fleet (1977) were refined with *LINUS* which minimizes  $\sum w(|F_o^2| - |F_c^2|)^2$ , where  $w^{-1} = \sigma^2(F_o^2)$ . The final agreement factors for the refinement, excluding the two strongly extinction-affected intensities 111 and  $2\bar{1}1$ , are summarized in Table 1.\* The exclusion of these two reflexions made no significant difference to the refined atomic parameters, which are presented in Table 2. Neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The cell dimensions were determined by a least-squares procedure from 13 high-angle ( $40 < 2\theta < 60^\circ$ ) reflexions. Mo *Kα*<sub>1</sub> ( $\lambda = 0.7093 \text{ Å}$ ) radiation was used. The results of the calculation of interatomic distances and angles are presented in Table 3.

The present refinement confirms the structure proposed by Westgren (1938) and Fleet (1977). However, it does differ from those investigations in the distribution of Ni–Ni and Ni–S distances.

Ni atoms occupy the distorted tetrahedral interstices of a slightly distorted body-centred cubic lattice (Fig. 1). The configuration of these occupied tetrahedral sites

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35066 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final agreement factors*

$R(F_o^2) = \sum   F_o^2  -  F_c^2   / \sum  F_o^2 $	0.053
$R_w(F_o^2) = [\sum w( F_o^2  -  F_c^2 )^2 / \sum w F_o^4 ]^{1/2}$	0.052
$R(F_o) = \sum   F_o  -  F_c   / \sum  F_o $	0.037
$S = [\sum w( F_o^2  -  F_c^2 )^2 / (m - n)]^{1/2}$	1.133

(where *m* = number of observations,  
*n* = number of parameters).

Table 2. Final fractional atomic coordinates and anisotropic thermal parameters ( $\times 10^4$ ), with e.s.d.'s in parentheses

Anisotropic temperature factors are defined as:  $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ .

		x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ni	(a)	$\frac{1}{2}$	0.2449 (2)	-y	162 (6)	124 (4)	$\beta_{22}$	2 (2)	$\beta_{12}$	4 (3)
S	(a)	0.2521 (2)	x	x	138 (5)	$\beta_{11}$	$\beta_{11}$	8 (4)	$\beta_{12}$	$\beta_{12}$

is such that the Ni atoms are no more than 2.53 Å apart.

Hazelwoodite consists of a series of triangular bipyramids (Fig. 1), with an Ni<sub>3</sub> triangle and S atoms at their apices. These Ni<sub>3</sub>S<sub>2</sub> units are interconnected through short Ni-S and Ni-Ni distances, the distances between the bipyramids being shorter than those within them. The Ni-Ni and Ni-S distances within the Ni<sub>3</sub>S<sub>2</sub> unit are 2.5319 (9) and 2.2914 (5) Å, whilst between them these distances are 2.4966 (4) and 2.2534 (5) Å respectively. This arrangement suggests some degree of repulsion between atoms in the Ni<sub>3</sub> triangles.

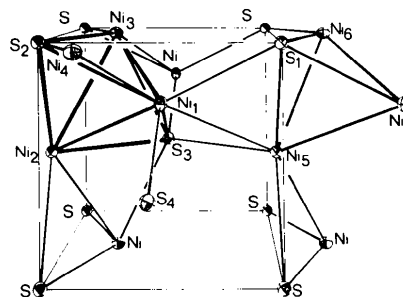
Several authors have argued that short metal-metal distances in metal-rich chalcogenides are indicative of metal-metal bonding, which gives rise to the stability of these materials. The present refinement confirms the

Table 3. Distances (Å) and angles (°) in Ni<sub>3</sub>S<sub>2</sub>

E.s.d.'s are in parentheses.

## Atomic positions

Ni(1)	x,	y,	z	Ni(7)	x,	y,	1 + z
Ni(2)	1 + z,	x,	y - 1	S(1)	x,	y,	z
Ni(3)	y,	1 + z,	x - 1	S(2)	x,	y,	z - 1
Ni(4)	y,	z,	x - 1	S(3)	1 - y,	1 - x,	-z
Ni(5)	1 + z,	x,	y	S(4)	1 - y,	-x,	-z
Ni(6)	y,	1 + z,	x				
Ni(1)-S(1)	2.2534 (5)	S(1)-Ni(1)-S(2)	127.25 (4)				
Ni(1)-S(2)	2.2914 (5)	S(1)-Ni(1)-S(3)	100.92 (2)				
Ni(1)-S(3)	2.2914 (5)	S(1)-Ni(1)-S(4)	102.94 (2)				
Ni(1)-S(4)	2.2534 (5)	S(2)-Ni(1)-S(3)	100.72 (2)				
Ni(1)-Ni(2)	2.5319 (9)	Ni(2)-Ni(1)-Ni(3)	60.00				
Ni(1)-Ni(3)	2.5319 (9)	Ni(2)-Ni(1)-Ni(4)	98.95 (1)				
Ni(1)-Ni(4)	2.4966 (4)	Ni(2)-Ni(1)-Ni(5)	108.13 (2)				
Ni(1)-Ni(5)	2.4966 (4)	Ni(3)-Ni(1)-Ni(4)	108.13 (2)				
S(1)-S(2)	4.0718 (6)	Ni(4)-Ni(1)-Ni(5)	148.73 (3)				
S(1)-S(3)	3.5051 (11)	S(2)-Ni(1)-Ni(4)	55.950 (6)				
S(1)-S(4)	3.5255 (4)	S(1)-Ni(1)-Ni(4)	101.71 (1)				
S(2)-S(3)	3.5291 (11)	S(1)-Ni(1)-Ni(3)	99.93 (3)				
		S(1)-Ni(1)-Ni(2)	155.04 (3)				
		S(4)-Ni(1)-Ni(4)	57.41 (3)				
		Ni(5)-S(2)-Ni(6)	67.07 (3)				
		Ni(1)-S(1)-Ni(6)	114.51 (3)				
		Ni(1)-S(1)-Ni(7)	127.25 (4)				
		Ni(1)-S(1)-Ni(5)	66.64 (2)				

Fig. 1. ORTEP (Johnson, 1965) drawing of Ni<sub>3</sub>S<sub>2</sub>. Labels refer to Table 3. The thick lines outline the Ni<sub>3</sub>S<sub>2</sub> units (see text).

presence in hazelwoodite of four short Ni-Ni distances, close to the Ni-Ni distance in metallic nickel (2.49 Å). This suggests that metal-metal interactions are important in stabilizing the structure.

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