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# The crystal structure of heazlewoodite, and metallic bonds in sulfide minerals

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## Abstract

Heazlewoodite ($Ni_3S_2$) is rhombohedral, space group $R32$, with unit cell parameters $a$ = 4.0821(5) Å, $\alpha$ = 89.475(9)° and one formula unit per unit cell. The crystal structure of its synthetic equivalent ($\alpha Ni_3S_2$) has been confirmed with X-ray powder intensity data (Fe$K\alpha$ radiation, $\lambda$ = 1.937 Å) and refined to a weighted residual index of 0.058. There are definitely four similar Ni–Ni 'bonds' per Ni atom, which is at variance with the theoretical treatment of Prewitt and Rajamani. However, this treatment is shown not to be applicable to sulfides, and possible reasons for this are discussed.

## Introduction

Heazlewoodite ($Ni_3S_2$) is rhombohedral with space group $R32$. The unit cell is dimensionally nearly cubic, having $a$ = 4.080 Å, $\alpha$ = 89.43° (Peacock, 1947), and contains one formula unit of $Ni_3S_2$. The crystal structure of its synthetic equivalent ($\alpha Ni_3S_2$) was determined by Westgren (1938) from qualitative X-ray powder intensity data and has Ni atoms in the 3$e$ equipoint position with $y$ = 0.25 and S atoms in the 2$c$ equipoint position with $x$ = 0.25. The S atoms form a slightly distorted body-centered cubic array, and the Ni atoms occupy distorted tetrahedral interstices. In addition to its four S neighbors, each Ni atom has four nearest neighbor Ni atoms, two at 2.48 Å and two at 2.51 Å. These Ni–Ni distances are similar to that in metallic Ni, and Hulliger (1968), Fleet (1972), and Prewitt and Rajamani (1974a) have argued that they indicate a significant degree of metallic bonding in heazlewoodite. Each S atom is coordinated to six Ni atoms. $Ni_3SSe$, $Ni_3Se_2$, and $(Ni,Co)_3S_2$ also crystallize with the heazlewoodite structure (Hulliger, 1968).

Recently, however, in spite of a qualitative confirmation by Peacock (1947), several authors have questioned the correctness of Westgren's structure determination. Pearson (1972) suggested that the heazlewoodite structure requires confirmation by single-crystal methods. Furthermore, Prewitt and Rajamani (1974a) have noted that the structure is inconsistent with their modification of Pearson's valence rule for intermetallic compounds, although they do admit the possibility that their theoretical argument might be based on an incorrect assumption. The present study is an attempt to resolve both the misgivings on the crystal structure of heazlewoodite and the inconsistency between the structure and Pearson's valence rule.

## Experimental

The crystal-structure investigation was made on synthetic $\alpha Ni_3S_2$, using X-ray powder diffraction data. A preliminary single-crystal precession camera investigation on natural heazlewoodite from the type locality, Trial Harbour, Tasmania, had shown that the crystallite mosaic spread in this material was far too great for the collection of meaningful intensity data. On zero-level precession films, reflections are rotated or spread about the film center by as much as 30°. However, the reflections are otherwise sharp, showing no tendency to be diffuse along radial directions or lattice rows, and thus giving no indication of disorder or lack of crystal perfection in the individual crystallites. This investigation on natural heazlewoodite also confirmed that the accepted space group ($R32$) is consistent with the diffraction symmetry. The systematic absences are just those associated with a rhombohedral unit cell indexed with hexagonal axes, giving the possible space group $R32$, $R3m$, and $R\bar{3}m$. However, $R3m$ and $R\bar{3}m$ are inconsistent with the heazlewoodite structure (see Discussion section).

Synthetic $\alpha Ni_3S_2$ was prepared by heating about 1.0 g of a stoichiometric mixture of Ni sponge and S crystals in an evacuated silica-glass tube at 700°C for one day and at 450°C for three weeks; the Ni sponge was reduced with hydrogen at 900°C before use. The unit-cell parameters, determined from a Jagodzinski focussing powder camera film (Fe$K\alpha_1$ radiation, $\lambda$ = 1.93597 Å) standardized with silicon, are $a$ = 4.0821 (5) Å, $\alpha$ = 89.475(9)°, standard deviations in parentheses, consistent with the data of Peacock (1947). Also, only heazlewoodite reflections are present on X-ray powder films. Hence the synthesized material is single-phase, stoichiometric $\alpha Ni_3S_2$, as would be expected from the available work on the phase relations of heazlewoodite (for example, Kullerud and Yund, 1962, and Misra and Fleet, 1973). Unfortunately the degree of crystal perfection was no better than that of the natural material, and in view of the lack of success of the iodine-vapor transport technique (Prewitt and Rajamani, 1974b), it was decided to abandon further attempts to obtain single crystals of the requisite quality. The reason for the difficulty in obtaining good quality single crystals of heazlewoodite is unclear. However, it may be associated with a phase transformation on cooling crystals grown at moderate temperatures (Prewitt and Rajamani, 1974b), or with the development of the rhombohedral distortion of the pseudocubic unit cell on cooling to room temperature, and study of heazlewoodite in a heating camera may throw some light on this problem.

Finely-ground synthetic $\alpha Ni_3S_2$ was held in a 0.2 mm diameter glass capillary tube and irradiated with Fe$K\alpha$ radiation for 48 hours in a 114.6 mm diameter Debye-Scherrer powder camera. The intensity data for the crystal-structure analysis were obtained from the powder film using a Joyce-Loebl densitometer, and were corrected for Lorentz and polarization effects, reflection multiplicity and absorption, and converted to observed structure factors ($F_o$). The Lorentz-polarization correction factor used was equated to the expression $(1+\cos^2 2\theta)/(\sin^2\theta\cos\theta)$, where $\theta$ is the Bragg diffraction angle, and reflection multiplicities were those of Laue class $\bar{3}m$. In making the absorption correction, the weight of $\alpha Ni_3S_2$ per unit volume in the capillary tube was determined, and this allowed the calculation of an effective linear absorption coefficient ($\mu$) of 280 cm$^{-1}$. Absorption correction factors ($A^*$) were estimated by graphical interpolation from the data for a cylindrical sample in *International Tables for X-ray Crystallography,* Vol. 2, Table 5.3.5B, using an effective $\mu R$ of 2.9. Weights were assigned proportionately to the corresponding observed intensities since, as a first approximation, the uncertainty in the intensity data must increase with decreasing peak/background ratio. The final data list contained 31 independent reflections, of which 27 had nonzero intensity.

## Crystal structure investigation

The crystal structure proposed by Westgren was refined by full-matrix, least-squares refinement using program RFINE (L. Finger, Geophysical Laboratory, Washington). RFINE minimizes the function $\Sigma w(|F_o|-|F_c|)^2$, where $w$ is the reflection weight, $F_o$ is the observed and $F_c$ the calculated structure factor, and calculates a conventional residual index, $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, and a weighted residual index $[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$. The scattering curve for $Ni^{2+}$ was taken from Cromer and Mann (1968), that for $S^{2-}$ computed for a nine-parameter fit from data in *International Tables for X-ray Crystallography,* and real and imaginary components of the anomalous dispersion coefficients for Ni and S were from Cromer (1965).

Using the reflections with nonzero intensity and unit isotropic thermal parameters for both Ni and S, the unrefined positional parameters of Westgren gave values for the weighted and conventional residual indices of 0.065 and 0.063, respectively. Refinement of the positional parameters converged on values for the weighted and conventional residual indices of 0.058 and 0.060, respectively, the weighted residual index being significant at the 0.05 level compared to that for unrefined positional parameters (Hamilton, 1965). The observed and calculated structure factors are given in Table 1, and the positional parameters are given in Table 2. Refinement of the isotropic thermal parameters reduced the weighted and conventional residual indices to 0.047 and 0.045, respectively. However, the refined thermal parameters for Ni and S are 1.13(17) and 0.05(26), respectively. Clearly, whilst the value for the Ni parameter may be meaningful, that for the S parameter largely reflects terminal errors in the data set. This is as expected, since terminal errors will be more significant with lighter atoms than heavier ones because of the smaller scattering contribution of the former. The low S thermal parameter does not reflect either error in the assumed chemical composition of $\alpha Ni_3S_2$, which is known to a far greater accuracy than is normally required for structural analysis, or incorrect space-group assignment (see following section).

## Discussion

Refinement of the structural positions with X-ray powder intensity data to a weighted residual index of 0.058 should represent adequate confirmation of the correctness of Westgren's structure for $\alpha Ni_3S_2$ and, hence, for heazlewoodite. Heazlewoodite has so few atoms per unit cell (one formula unit of $Ni_3S_2$) that an incorrectly positioned atom in the structure would give an anomalously high residual index. It follows that the correct space group for heazlewoodite is the accepted one, *R*32. *R*3*m* does not allow a similar structure. $R\bar{3}m$, with S in 2*c* and Ni in 6*g* equipoint positions, would allow a disordered heazlewoodite structure, but this also would give a significantly high residual index and has prohibitively short Ni–Ni distances (2.04 Å, 1.44 Å).

The heazlewoodite structure is based on a body-centered cubic array of S atoms with Ni atoms in three of the twelve sphenoidal (near-tetrahedral) sites per unit cell. The ordered arrangement of Ni atoms in the ideal structure is shown in Figure 1. The $NiS_4$ 'tetrahedra' share four edges, giving rise to four short Ni–Ni distances per Ni atom. As mentioned earlier, the structure does not permit disordering of the Ni atoms.

Selected bond distances and bond angles with some comparative data for the ideal, dimensionally cubic structure are given in Table 3. In the refined structure, the S environment about each Ni atom is still decidedly sphenoidal, but the four Ni atoms completing the nearest-neighbor Ni coordination polyhedron do not even approximate to a tetrahedral disposition. The S coordination polyedron is a distorted trigonal prism, with three bonded Ni atoms at one end and three nonbonded Ni atoms at the other. The two nonequivalent Ni–S bond distances and the two nonequivalent short Ni–Ni distances in the refined structure are not significantly different from the respective equivalent distances in the ideal dimensionally-cubic structure. However, the S–Ni–S bond angles associated with shared edges are all shorter than the ideal values, which is consistent with some degree of repulsion between the polyhedral edge-related Ni atoms.

The short Ni–Ni distances in heazlewoodite are only slightly greater than that for metallic Ni (2.492 Å), and if interatomic distance in these materials is correlatible with bond strength, they would have to be regarded as equivalent to full metallic bonds. A structure refinement based on single-crystal data, which may not be realized until advances have been made in crystal-growing techniques, would reduce

Table 1. Observed and calculated structure factors for synthetic heazlewoodite

| h | k | l | $F_o$ | $F_c$ | h | k | l | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | 22.0 | 24.5 | 2 | 2 | -1 | 15.8 | 15.1 |
| 1 | 1 | 0 | 0.0 | 1.4 | 2 | 1 | -2 | 15.8 | 15.8 |
| 1 | 0 | -1 | 45.2 | 47.1 | 3 | 1 | 0 | 26.1 | 28.5 |
| 1 | 1 | 1 | 57.4 | 62.0 | 3 | 0 | -1 | 0.0 | 1.8 |
| 1 | 1 | -1 | 22.5 | 20.5 | 3 | 1 | 1 | 9.8 | 11.4 |
| 2 | 0 | 0 | 39.6 | 38.0 | 3 | 1 | -1 | 13.2 | 14.8 |
| 2 | 1 | 0 | 41.5 | 43.4 | 3 | -1 | -1 | 40.3 | 40.4 |
| 2 | 0 | -1 | 41.1 | 40.5 | 2 | 2 | 2 | 21.6 | 25.8 |
| 2 | 1 | 1 | 36.7 | 33.1 | 2 | 2 | -2 | 22.5 | 25.1 |
| 2 | 1 | -1 | 48.5 | 47.1 | 3 | 2 | 0 | 25.0 | 26.1 |
| 2 | -1 | -1 | 37.0 | 35.4 | 3 | 0 | -2 | 26.9 | 27.4 |
| 2 | 2 | 0 | 0.0 | 1.2 | 3 | 2 | 1 | 36.7 | 33.6 |
| 2 | 0 | -2 | 0.0 | 1.7 | 3 | 2 | -1 | 25.2 | 24.3 |
| 2 | 2 | 1 | 15.9 | 16.7 | 3 | 1 | -2 | 37.0 | 34.4 |
| 3 | 0 | 0 | 15.8 | 15.1 | 3 | -1 | -2 | 24.8 | 22.7 |
|  |  |  |  |  | 4 | 0 | 0 | 42.3 | 43.5 |

Table 2. Positional parameters for synthetic heazlewoodite (standard deviations in parentheses)

| Atom | Equipoint Position | x | y | z |
|---|---|---|---|---|
| Ni | 3e | 1/2 | 0.247(2) | -y |
| S | 2c | 0.255(3) | x | x |

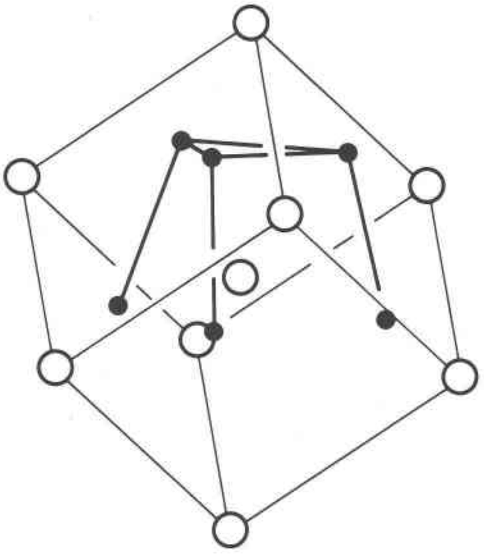

Fig. 1. Ideal, dimensionally cubic structure of heazlewoodite showing the body centered cubic array of S atoms and distribution of the short Ni–Ni distances: open circles; S atoms: full circles; Ni atoms: unit cell origin on S atom at *x* = ¾, *y* = ¾, *z* = ¾.

Table 3. Interatomic distances (Å) and bond angles (degrees) in synthetic heazlewoodite (standard deviations in parentheses) with some comparative data for the ideal undistorted structure ($a$ = 4.0821 Å)

| Bond | Bond Multiplicity | Distance | Ideal Distance | Bond Angle | Bond Angle Multiplicity | Angle | Ideal Angle |
|---|---|---|---|---|---|---|---|
| Ni-S | 2 | 2.27(2) | 2.28 | S-Ni-S' | 2 | 127.8(6) | 126.9 |
| -S' | 2 | 2.27(2) | | S-Ni-S'' | 2 | 100.7(3) | 101.5 |
| -Ni' | 2 | 2.52(2) | 2.50 | S-Ni-S''' | 1 | 100.6(9) | |
| -Ni'' | 2 | 2.51(2) | | S'-Ni-S'' | 1 | 102.6(5) | |
| S-S' | 6 | 4.0821(5) | 4.08 | Ni'-Ni-Ni'' | 2 | 108.6(4) | |
| -S'' | 3 | 3.50(2) | 3.54 | Ni'-Ni-Ni''' | 2 | 99.2(2) | |
| -S''' | 1 | 3.50(5) | | Ni'-Ni-Ni'$^{\mathrm{v}}$ | 1 | 60.0 | |
| S'-S'' | 3 | 3.55(2) | | Ni''-Ni-Ni''' | 1 | 147.9(6) | |
| | | | | Ni-S-Ni' | 3 | 67.2(7) | |
| | | | | Ni-S-Ni''' | 3 | 67.0(2) | |
| | | | | Ni-S-Ni$^{\mathrm{v}}$ | 3 | 112.6(5) | |

| | | | | |
|---|---|---|---|---|
| Atomic Positions: | Ni | .5,.247,.753 | S | .255,.255,.255 |
| | Ni' | .753,.5,.247 | S' | .255,.255,1.255 |
| | Ni'' | .753,.5,1.247 | S'' | .745,-.255,.745 |
| | Ni''' | .247,-.247,.5 | S''' | .745,.745,.745 |
| | Ni'$^{\mathrm{v}}$ | .247,.753,.5 | | |
| | Ni$^{\mathrm{v}}$ | -.247,.5,.247 | | |

the estimated standard deviations of the Ni–Ni distances and, hence, might show that Ni–Ni′ is significantly shorter than Ni–Ni″ (Fig. 2). Nevertheless, the bond strengths associated with both distances would remain effectively the same. Any hypothesis on the nature of the metal–metal interactions in chalcogenides must consider that in heazlewoodite there are four effectively equivalent Ni–Ni interactions per Ni atom. Hence, having established the heazlewoodite structure, it remains to explain the apparent inconsistency between it and the modified valence rule of Prewitt and Rajamani (1974a).

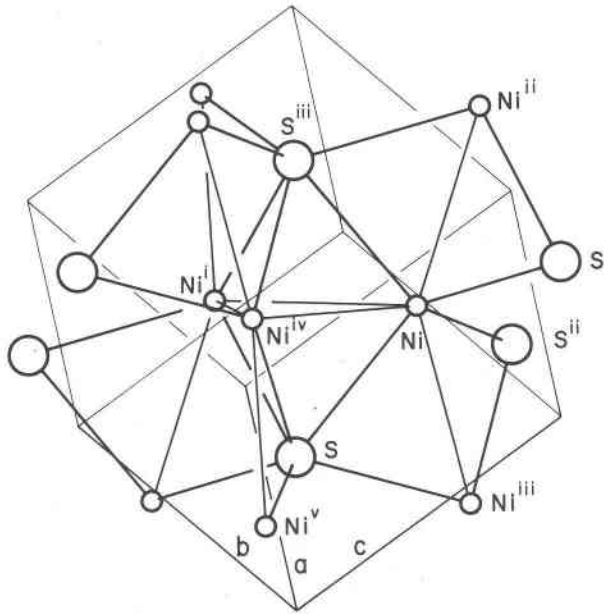

Fig. 2. Crystal structure of heazlewoodite showing coordination polyhedra of Ni and S: S atoms; large open circles: Ni atoms; small open circles.

The valence rule introduced by Mooser and Pearson (1960) and discussed by Pearson (1972) suggests that intermetallic valence compounds must satisfy the condition $(n_a + n_c + b_a - b_c)/N_a = 8$, where $n_a$ is the number of $s$ and $p$ valence electrons on the ligand atoms (anions), $n_c$ is the number on the metal atoms (cations) less any unshared valence electrons, $b_a$ is the number of electrons involved in forming ligand–ligand bonds, $b_c$ is the number of electrons forming metal–metal bonds, and $N_a$ is the number of ligand atoms. It is assumed that all ligand–ligand and metal–metal bonds are electron-pair ones. The usefulness of this rule is somewhat limited, and it certainly cannot be used to confirm a possible structural arrangement; for example, Pearson (1972) successfully applied the rule to monoclinic $ZnP_2$, assuming it to be both polyanionic and polycationic, yet this compound has been shown recently to be only polyanionic (Fleet, 1974).

Prewitt and Rajamani (1974a) modified the Mooser-Pearson valence rule to predict the number of single-bonded metal bonds ($C_c$) per metal atom in sulfide compounds. Thus $C_c = (n_a + n_c + C_aN_a - 8N_a)/N_c$, where $n_c$ is redefined as the number of valence plus unpaired antibonding *d* electrons on the metal atoms, $C_a$ is the number of ligand–ligand bonds per ligand, and $N_c$ is the number of metal atoms. Prewitt and Rajamani argue that this modified rule successfully predicts the number of metal bonds in mackinawite $[(6 + 6 + 0 - 8)/1 = 4]$, cobalt pentlandite $[(8 \times 6 + 8 \times 5 + 0 - 8 \times 8)/8 = 3]$, and millerite $[(6 + 4 + 0 - 8)/1 = 2]$. Therefore, the predicted number of metal bonds in heazlewoodite $[(2 \times 6 + 3 \times 4 + 0 - 16)/3 = 2.67]$ cast doubt on the reliability of the crystal structure determination. However, in the calculations for cobalt pentlandite the octahedral Co atom cannot be ignored, since the S atoms contribute valence electrons to the $\mathrm{Co}\underset{\mathrm{oct}}{-}\mathrm{S}$ $\sigma$ bonds, and hence for the tetrahedral cobalt atoms, $C_c > 3$. Also, where agreement with the rule is obtained no cognisance is taken of the stereochemical properties of the *d* orbitals involved. It is assumed that the antibonding 3*d* orbitals on the metal atoms form the bonding orbitals for the metal bonds. As discussed by Fleet (1973a and b), in studies on metal–metal interactions in, respectively, maucherite and parkerite, these antibonding orbitals naturally project along or close to the metal–ligand $\sigma$ bonding directions and are very often poorly disposed spatially to participate in the metal–metal bonds. In contrast, the spatial distribution of the nonbonding set of 3*d* orbitals will very often allow for end-on overlap to form metal–metal $\sigma$ bonds. However, in many minerals, all of the nonbonding electrons would be paired if the metal–ligand complexes were isolated, and some of these electrons must be removed for bonding interactions to take place.

Rajamani and Prewitt (1974) and Prewitt and Rajamani (1974a) assumed that all of the metallic bonds they discussed were equivalent to single bonds—that is electron-pair bonds. There is, of course, no logical reason why this should be the case, especially since this is apparently not a requirement of the metal–ligand $\sigma$ bonds, and metal–metal 'bonds' do show a wide variation in bond length in chalcogenides. Prewitt and Rajamani (1974a) have suggested that this assumption might be incorrect and thus be the explanation for the lack of agreement between the calculated and 'observed' number of metal bonds in heazlewoodite.

In summary, the modified valence rule has not been demonstrated to apply to chalcogenide minerals in general. The theoretical basis for it is unsound, and thus it cannot be used as a check on the reliability of the crystal structure of heazlewoodite.

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