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High-pressure crystal chemistry of nickel sulphides

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Abstract

Monochromatic synchrotron x-ray diffraction data collected at CHESS and ESRF at varying temperatures and pressures were used to investigate the crystal structures of phases with the composition Ni_3S_2 . At low pressures Ni_3S_2 has the rhombohedral heazlewoodite structure (Ni_3S_2 I), but transforms to two new structures at higher pressures and temperatures. Ni_3S_2 III is orthorhombic (space group $Cmcm$, $a = 3.118 \text{ \AA}$, $b = 10.862 \text{ \AA}$, $c = 6.730 \text{ \AA}$) and contains Ni coordinated by five S atoms in a square pyramid. The structure of Ni_3S_2 III is described in this report along with an analysis of electronic structures of nickel sulphides.

1. Introduction

The coupling of diamond-cell and synchrotron diffraction techniques together with increasing interest in high-pressure phases of geological importance has led to a number of investigations of transition metal oxides, sulphides, and phosphides at high pressures. We report here the results of experimental and theoretical studies of nickel sulphides that illustrate how the structures of these materials differ from each other.

2. Experimental details

In high-pressure experiments, we collected diffraction data at the CHESS F2 station and later at the ESRF beamline ID30 on polycrystalline Ni_3S_2 at pressures up to 23 GPa and temperatures up to 342 °C, using an imaging plate area detector. In the first series of experiments at CHESS we began with Ni_3S_2 in the rhombohedral heazlewoodite structure (Ni_3S_2 I). The sample was compressed without a pressure medium in an externally heated diamond-anvil cell (DAC). The sample began to transform to a second phase (Ni_3S_2 II) as the pressure was raised to about 20 GPa at 20 °C. The two phases coexisted with increasing pressure to 23 GPa. Then the temperature was raised to 189 °C where Ni_3S_2 I disappeared and a third phase (Ni_3S_2 III) appeared. This was the last CHESS experiment, but the sample was kept in the DAC

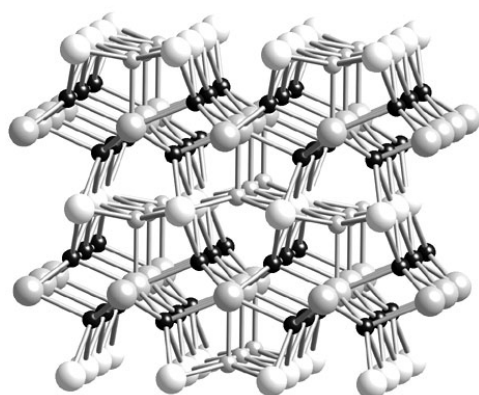


Figure 1. Crystal structure of Ni₃S₂ III.

Table 1. Interatomic distances in Ni₃S₂ III.

Ni1–S1	2.334 Å (X4)	Ni1–Ni2	2.536 Å (X2)
Ni1–S2	2.252 Å (X1)	Ni1–Ni1	2.512 Å (X2)
Ni2–S1	2.404 Å (X2)	Ni1–Ni1	3.116 Å (X2)
Ni2–S2	2.217 Å (X2)	Ni2–Ni2	2.624 Å (X2)
Ni2–S2	2.329 Å (X1)	Ni2–Ni2	2.448 Å (X1)

Table 2. Atom coordinates for Ni₃S₂ III.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ni1	0	0.5388	1/4
Ni2	0	0.3375	0.0685
S1	0	0	0
S2	0	0.7457	0.25

until the experiments at ESRF began. Here the temperature was raised to 342 °C without adjusting the cell pressure, which was still at 23 GPa when heating began. At about 242 °C Ni₃S₂ II disappeared and the pattern contained just diffraction lines from Ni₃S₂ III and the Au internal standard, and Ni₃S₂ III remained as the only sulphide phase when the sample was returned to room temperature. The powder pattern of this material obtained at 15 GPa and room temperature was indexed using the program Jade [1] and its structure solved with the program Endeavour [2]. Preliminary Rietveld refinement was conducted with GSAS [3]. Ni₃S₂ III is orthorhombic (space group *Cmcm*, $a = 3.118$ Å, $b = 10.862$ Å, $c = 6.730$ Å) and contains Ni coordinated by five S atoms in a square pyramid (SP), which shares two triangular faces with Ni2 SPs, two edges with Ni1 SPs, and two edges with Ni2 SPs. Ni2's SP shares one triangular face with a Ni1 SP, three edges with Ni2 SPs, and one edge with Ni1 SP. Ni₃S₂ III also has very short Ni–Ni distances ranging from 2.45 to 2.62 Å, comparable to the distance in Ni metal, 2.49 Å, at 1 atm. The basic chain of SPs in HP Ni₃S₂ is very similar to that in millerite (NiS) except that the linking to adjacent chains is different. In millerite, there is a SP that shares four edges and two corners with other identical SPs. The structure of Ni₃S₂ III is shown in figure 1 and the atom coordinates and interatomic distances are given in tables 1 and 2.

Because of overlap of the patterns of Ni₃S₂ II with those of Ni₃S₂ I and III, it was not possible to obtain an unequivocal indexing of Ni₃S₂ II. Thus, we are not able to provide cell or structural data on this phase at present.

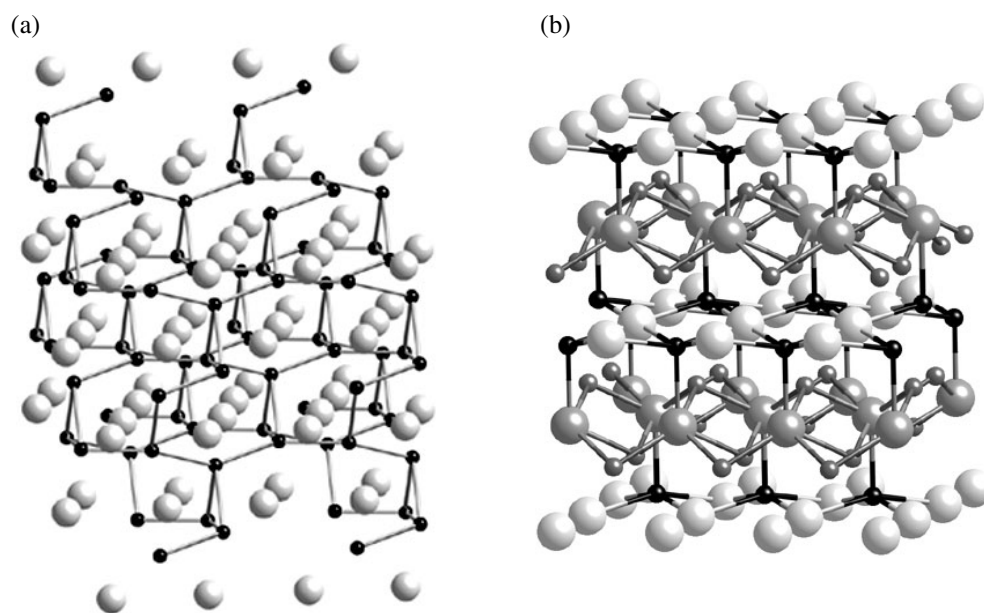


Figure 2. (a) Coordination environment about Ni atoms in heazelwoodite, emphasizing the interconnected Ni_3 triangles. Ni atoms: dark spheres; S atoms: light spheres. (b) Perspective view of the crystal structure of the high-pressure phase of Ni_3S_2 , illustrating the alternation of the millerite-like layers with the alloy-like layers. Small spheres, Ni atoms; large spheres, S atoms. For Ni: dark spheres, Ni1; light spheres, Ni2. For S: light spheres, S1; dark spheres, S2. A: $[\text{NiS}]^0$ layer; B: $[\text{Ni}_2\text{S}]^0$ layer.

3. Electronic structures of heazelwoodite and high-pressure Ni_3S_2

The two Ni_3S_2 polymorphs present an intriguing problem in the crystal structure and bonding of inorganic solids, and illustrate the surprising effects that pressure may have upon the electronic structure. At low pressure, the heazelwoodite structure [4] contains an interconnected network of Ni_3 triangles directly connected to each other by Ni–Ni bonds, as shown in figure 2(a).

Sulphur atoms are arranged in hexagonal layers stacked one directly above the other along the a -direction of the unit cell. Each Ni atom is bonded to two Ni atoms from two other Ni_3 triangles, and then to the other two Ni atoms in the same triangle, giving each Ni atom a tetrahedral coordination environment with two nearly identical Ni–Ni distances. The relatively long S–S distances (4.08 Å within the layer, and 3.52 Å between layers) also show quite clearly that the sulphur atoms may be considered as isolated sulphide ions, taking two electrons each from the Ni_3 framework, which then may be considered an infinite transition metal cluster.

Each Ni atom has ten valence electrons to provide to the Ni_3 cluster, for a total of 30. According to the rules for electron counting in clusters proposed by Wade [5], the Ni_3 cluster requires $(n + 1)$ skeletal bonding electrons for stability, where $n = 5$, since the triangle is actually considered an ‘arachno’-trigonal bipyramid, that is, a trigonal bipyramid with two vertices removed. In other words, any triangular cluster will require enough electron pairs to keep it stable as a trigonal bipyramid; this accounts for 12 electrons in the $(n + 1)$ pairs. Now, each Ni atom must offer two electrons for direct Ni–Ni bonding, in the first approximation, for the two Ni–Ni bonds joining it to other Ni_3 clusters (exocyclic bonds), accounting for six more electrons from the cluster. Finally each Ni_3 cluster must also donate four electrons to

stabilize the two sulphur atoms, given the fact that they are isolated in the structure. This leaves a total of eight electrons to be placed in non-bonding cluster orbitals and an average oxidation state of 4/3 for the nickel atoms, leading to a prediction of paramagnetic and perhaps metallic behaviour in heazelwoodite. Observation of the latter would depend upon the degree of orbital overlap between individual Ni₃ units provided by the exocyclic Ni–Ni bonds.

At high pressure, the most important changes in the heazelwoodite structure take place in the array of isolated sulphide ions. Under pressure, the two separate S–S distances in heazelwoodite promote the formation of two distinct, interconnected layers that characterize the high-pressure structure of Ni₃S₂ III, as shown in figure 2(b).

In one plane (A), the sulphur atoms form a nearly square net; in fact, the S–S distances (3.12 Å along the *a*-direction and 3.37 Å along *c*) suggest that the topology is actually an overlap of one-dimensional sulphur chains to form a ladder structure, where the chain/ladder direction is defined by the shorter S–S distance. Each section of the ladder forms the basal plane of a nearly regular SP about a nickel atom, where the metal atoms sit slightly above the plane. The S–S distances, however, are quite long compared to a covalent S–S bond (2.09 Å in pyrite-type NiS₂), indicating that the sulphur atoms are still best considered as isolated sulphide ions. Electron counting [6] shows that covalently bonded linear chain/ladder or square net structures are stabilized by electron counts of six electrons per atom, which would leave the formal charge of planes of sulphur atoms at zero. It is therefore clear that the effect of pressure on this portion of the structure has been to organize the sulphur atoms into an array that will eventually transfer charge from the sulphur atoms to the nickel atoms at higher pressures. A second plane of sulphur atoms (B) is formed from the same linear sulphur chains with S–S distances of 3.12 Å along *a*, except that the chains in this layer are not aligned, but instead are staggered so as to form a hexagonal net of sulphide ions. Sulphur atoms in the B layer then provide the apical ligands for the square pyramidal coordination of nickel atoms associated with the sulphur atoms in plane A. These one-dimensional chains of edge-sharing SPs represent effectively an unfolding of the trinuclear clusters of the millerite structure of NiS [7]. A comparison of the crystal structure and properties of the millerite phase as well as those of BaNiS₂ [8] to the structure of Ni₃S₂ III suggests that the coordination around the nickel atom in this high-pressure phase corresponds to a typical Ni²⁺ environment for sulphides, and leads to a description of the A layer as [NiS]⁰. This is particularly evident since the Ni–S distances in the coordination polyhedra of Ni₃S₂ III are nearly the same as those in millerite and BaNiS₂, despite the fact that the former is a high-pressure phase. The B layer of the Ni₃S₂ III structure is then a metal-rich layer with stoichiometry [Ni₂S]⁰, leading to the assignment of the nickel atoms as the reduced oxidation state of Ni¹⁺. Nickel atoms in this layer are also five-coordinated by sulphur, but the coordination is significantly more irregular than for the Ni in the adjacent layer as a result of the hexagonal arrangement of the sulphide ions as opposed to the square arrangement found in layer A.

Comparing the structures of the two phases of Ni₃S₂, it becomes apparent that the effect of pressure on the heazelwoodite structure has been to induce a charge disproportionation of the nickel atoms:



which arises from the reorganization of the sulphide array present in heazelwoodite. Surprisingly, this reorganization of the sulphide ions has allowed the typical square pyramidal coordination of Ni²⁺ to appear at high pressure, where a shift to lower oxidation states might be expected. A combination of the metal-rich stoichiometry of Ni₃S₂ and the stability of the purely hexagonal array of the sulphide ions dictates that the square pyramidal Ni²⁺ coordination environment is therefore not observed in the low-pressure phase.

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