ON THE UNUSUAL ARRANGEMENT
OF METAL ATOMS IN PENTLANDITE

V. V. Bakakin and V. A. Drebushchak

Pentlandite is cubic sulfide of iron, nickel, and cobalt. The exact metal to sulfur ratio is still unknown. Structure solution for this mineral gave a composition MgS$_8$ [1]. However, synthesis at the center of the Fe–Ni–S system unambiguously indicates an increased content of the metal. Synthetic samples were ascribed the compositions M$_{9.117 \pm 0.046}$S$_8$ and M$_{9.127 \pm 0.014}$S$_8$ for Fe:NI $= 5.8:3.3$ and $3.1:6.1$, respectively [2].

The aim of this work is to correct the crystal-chemical treatment of pentlandite using a geometrical model approach and assuming that the metal/sulfur ratio exceeds 9:8 due to an excess of metal atoms but not a lack of sulfur atoms. The purpose of this correction is inclusion of additional metal atoms in the structure of pentlandite.

Sulfur atoms form a slightly distorted cubic closest packing. Figure 1a shows a fragment of the structure (two unit cell octants) — two “small” face-centered cubes of sulfur atoms. The S1 atoms lie at the vertices, and the S2 atoms center the faces. Inside the upper cube (below “cube O”) is an octahedrally coordinated metal atom (M$^{[6]}$) surrounded by eight empty tetrahedra. The lower cube (below “cube T$_8$”) contains eight metal atoms (M$^{[1]}$) of the tetrahedra around the empty octahedron. The tetrahedra share three edges with one another and form an island cluster with a cubic configuration due to shortened M$^{[1]}$–M$^{[1]}$ contacts (~2.5 Å). The $O$ and $T_8$ cubes alternate in a way similar to alternation of Na and Cl in the structure of NaCl.

In an idealized structure of pentlandite, the number of the $O$ and $T_8$ cubes is the same, and each cube contains four sulfur atoms. The crystal-chemical formula of pentlandite is M$_{[6]}$S$_4$. M$_{[1]}$S$_4$ or, when written in more customary form, M$^{[6]}$M$^{[1]}$S$_8$. For the idealized pentlandite, the metal/sulfur ratio is 9:8.

For any sulfur packing analogous to cubes in pentlandite, there is one more, also widespread, scheme of metal arrangement in tetrahedral coordination. It is met in sphalerite (ZnS), chalcopyrite structures (M$_{16+x}$S$_{16}$, $x = 1, 2$), and thiospinels M$_3$S$_4$ (Fig. 1b). This exhausts all currently known configurations.

![Fig. 1. Arrangement of metal atoms in face-centered cubes of sulfur atoms: a) octahedral (O) and tetrahedral (T$_8$) configurations in pentlandite; b) tetrahedral (T$_4$) configuration in sphalerite; c) hypothetical tetrahedral (T$_2$) configuration in pentlandite.](image-url)
Additional metal atoms may not be located in the structure of pentlandite in the framework of the accepted model. We believe they may be placed at the tetrahedral sites of the $O$ cube. For this purpose, an atom must leave its octahedral position at the center and shift by $2.2 \AA$ to a position on the other side of any octahedral face. Another metal atom may be inserted at the opposite tetrahedral position at a distance of $4.4 \AA$ in the same cube. This cube is designated as $T_2$ (Fig. 1c). Figure 2 shows a fragment of the structure with violated alternation of cubes, with the $T_2$ cube instead of the $O$ cube lying at the center of the fragment. As the $T_2$ cube is formed from the $O$ cube, the overall number of these cubes is constant and equals the number of $T_8$. The fraction of $O$ cubes transformed into $T_8$ is denoted by $x$. Then the composition of pentlandite is $(1-x)\cdot M_{[0]}^4 S_4\cdot x\cdot M_{[t]}^4 S_4\cdot M_{[8]}^8 S_4$ or $M_{[t]}^4 M_{[2x]}^8 M_{[8]}^8 S_8$. The metal/sulfur ratio in this pentlandite is $(9+x):8$.

The structural model of pentlandite with three types of cube ($T_8$, $T_2$, and $O$) instead of two types ($T_8$ and $O$) makes it possible to explain the excess of metal.

The physicochemical properties of pentlandite give us reason to argue that the $T_2$ cube exists in reality. It was established experimentally that the ratio between the iron atoms at the octahedral and tetrahedral sites decreases after heating the sample to $200^\circ C$. This was explained by the preferable occupation of octahedral positions by Fe atoms at decreased temperatures and by Ni atoms at elevated temperatures [1]. The micromechanism of this cation substitution (and atomic displacement) was not examined previously.

We propose the following scheme of substitution. The only way for the metal atom (let it be Fe for the present case) to abandon the octahedral position is to occupy one of the tetrahedral vacancies in the same cube. In terms of $O$ and $T$ cubes this elementary act may be interpreted as formation of a $T_1$ cube from the $O$ cube:

I. $O \rightarrow T_1$.

The distance between the tetrahedral position in the $T_1$ cube and that in the neighboring $T_8$ cube is shorter than any distance inside the $T_8$ cube, since $M_{[t]}^1 S_1$ is shorter than $M_{[t]}^8 S_2$ [1]. Thus favorable conditions are created for a transition of the metal atom from $T_8$ to the neighboring $T_1$ cube:

II. $T_8 + T_1 \rightarrow T_7 + T_2$.

Here $T_7$ denotes the $T_8$ cube with an open position. The lifetime of the vacancy is finite, and some time later the position will again be occupied by the metal atom from the neighboring $T_2$ cube:

III. $T_7 + T_2 \rightarrow T_8 + T_1$.

The only atom left will occupy an octahedral position:

IV. $T_1 \rightarrow O$.

Now we come back to the initial situation with $O$ cubes neighboring $T_8$. However, the nickel atom left the $T_8$ cube in step II, the vacancy in $T_7$ was occupied by an iron atom in step III, and the nickel atom remained in the

![Fig. 2. Fragment of the structure of pentlandite. The $O$ cube at the center is replaced by $T_2$.](image)