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A STRUCTURAL PROPOSAL FOR BOULANGERITE

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ABSTRACT

A structure for the sub-cell of boulangerite is proposed which explains the morphology (as needles) and shows the boundary between the "galena-like" and the "stibnite-like" structures of complex sulfides.

The last reported research on boulangerite was by Berry (1940), who made Weissenberg photographs. If the weak first layer is neglected, the unit cell can be taken as

$$a_0 = 21.14, \quad b_0 = 23.46, \quad c_0 = 4.035 \text{ Å}; \quad \text{space group } Pbnm.$$

Including the weak first layer, Berry proposed a monoclinic cell, or an orthorhombic *B* cell, the latter with doubled *a* and *c* axes.

This paper gives the result of a structure determination for the sub-cell of boulangerite. The specimen used was labelled "Heteromorphit" or "Federerz" = "plumosite," from Pribram, Bohemia.* Weissenberg photographs of the 0 and 2nd level were similar to those published by Berry, and with respect to the sub-cell there is full agreement with his results. However the weak first level on our film shows orthorhombic symmetry, and not the monoclinic symmetry shown by Berry's photograph.† Nevertheless, the differences in the intensities of related reflections are slight in Berry's photograph, and therefore we prefer the orthorhombic symmetry for the large unit cell with

$$a_0 = 42.28, \quad b_0 = 23.46, \quad c_0 = 8.07 \text{ Å}; \quad \text{space group } Bb2_1m$$

The chemical analysis by Berry leads to the formula $Pb_{20}Sb_{16}S_{44}$ for the sub-cell, which is also the basis for our structure determination. The calculations were made on an IBM 650 machine, using the INCOR program (by Zalkin/Jones, 1957); the least-squares program (by Templeton/Senko, 1957); and the Patterson-Fourier-Program (Darmstadt-Sindelfingen-Program). A proposed structure for the metal atoms was derived from two Patterson sections $P(u, v, o)$ and $P(u, v, \frac{1}{2})$. With the aid of these metal positions a Fourier synthesis was calculated; this Fourier synthesis also gave the positions of most of the sulfur atoms. During the least-squares refinement the remaining sulfur atoms were located.

Both the first layer and the very weak reflections of the 0 and 2nd layer were neglected in the first estimation of the structure, because the

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† Professor L. G. Berry kindly sent us his film.

Weissenberg photographs showed a large anisotropic influence of the absorption factor, and in addition these weak reflections are influenced by the superstructure. Table 1 shows the estimated parameters of boulangerite which gave an R-factor of 17.6%. This seems unexpectedly favorable in view of the neglect of the weak reflections.

Boulangerite has 3 positions occupied by Pb and 3 by Sb. Positions 4–6 are occupied in the sub-cell by a statistical distribution of Pb and Sb with the atomic form factor $(f_{Pb}+f_{Sb})/2$. This is reasonable for the superstructure and indicates in this case that Pb and Sb alternate in the *c* direction. Position 9 was split up in two antimony atoms, which were shown by the Fourier synthesis. Therefore the atomic form factor for 9*a* and 9*b* has the value of $f_{Sb}/2$. We recognize this splitting by the strong deviation of the temperature factors from the average of all the other atoms.

TABLE 1. ATOMIC PARAMETERS OF BOULANGERITE

Number of Atom	Symbol	Parameter		
		x	*y*	*z*
1	Pb	0.307	0.160	0.250
2	Pb	117	498	250
3	Pb	206	323	250
4	Pb, Sb	458	433	750
5	Pb, Sb	132	098	750
6	Pb, Sb	486	129	750
7	Sb	287	462	750
8	Sb	046	232	250
9*a*	Sb/2	388	283	750
9*b*	Sb/2	372	307	750
10	S	069	017	250
11	S	247	028	250
12	S	156	175	250
13	S	420	219	250
14	S	330	375	250
15	S	372	088	750
16	S	014	138	750
17	S	278	251	750
18	S	096	295	750
19	S	186	415	750
20	S	013	441	750

In contrast to Berry's formula $Pb_{20}Sb_{16}S_{44}$, our rough structure estimation for the sub-cell indicates a formula $Pb_{18}Sb_{18}S_{44}$. The later refinement for the superstructure and the calculation of the anisotropic absorption factor may change our formula in the direction of Berry's formula. Figure 1 shows the result of the structure determination; the hatched parts indicate the chains in the *c* direction, which are responsible for the plumose morphology.

A first proposal to derive the structure of complex sulfides from the galena (NaCl) type was made by Hofmann (1935) and extended by Hellner (1958). A number of sulfides, like miargyrite, meneghinite, cosalite, and the andorite group follow this pattern and it was shown that it is possible to extend it also to stibnite, but it was mentioned that the coordination number of the metal atoms increases from 6 to 7 in stibnite.

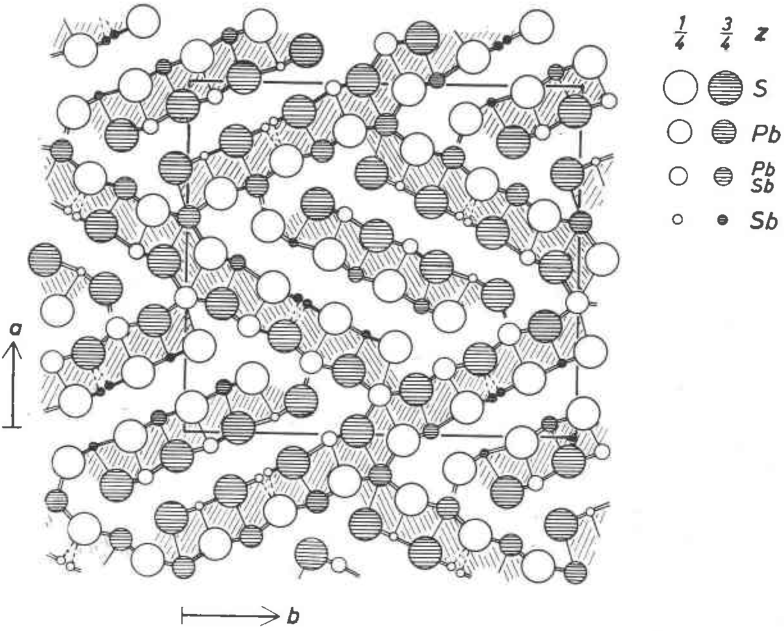

FIG. 1. Structure of boulangerite for the sub-cell, projected on (001); the hatched parts indicate the chains in the *c*-direction.

Figure 2 shows an ideal galena type, projected on (110). In Fig. 3 the atoms have the same *x* and *y* parameter, but the *z* parameters of half of the atoms are interchanged in such a way that the coordination number of the metal atoms becomes 5+2 (=7), the latter with a larger distance. The 3-dimensional network of the galena structure (Fig. 2) has been divided into 2-dimensional nets. This change from a galena-like structure to a net structure can be considered to be produced by a large replace-

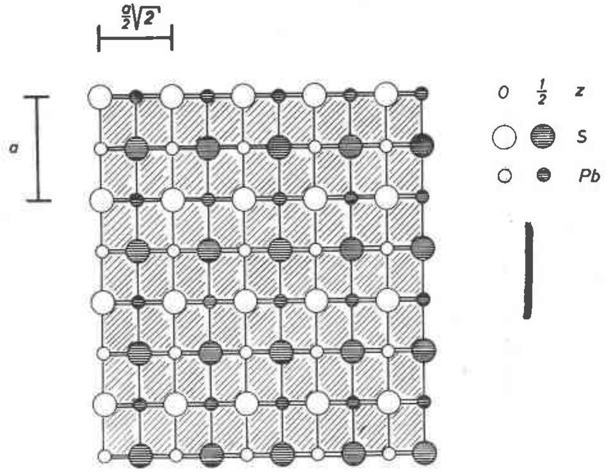

FIG. 2. Structure of the galena (NaCl) type, projected on (110).

ment of Pb and Sb. But hand in hand with this replacement the ratio between metal and sulfide atoms decreases and the nets are cut off into chains of variable width in respect to the two factors mentioned above. Typical representatives of this group are jamesonite (Niizeki and Buerger, 1957*b*) and boulangerite.

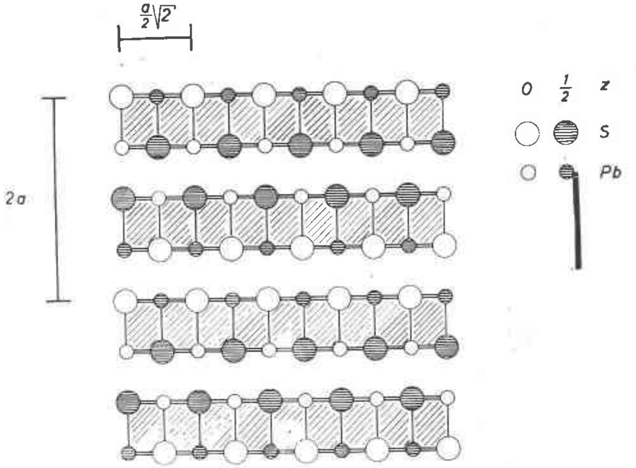

FIG. 3. Projection of the galena type on (110), but half of the *z* parameters of the sulphur and metal atoms are interchanged in such a way that the 3-dimensional network of the galena type changes into 2-dimensional infinite nets. The coordination number changes from 6 in the galena type to 5+2(=7) in the "net" structure. These nets are cut off in chains in respect to the *c*-direction, as we can find in boulangerite and jamesonite.

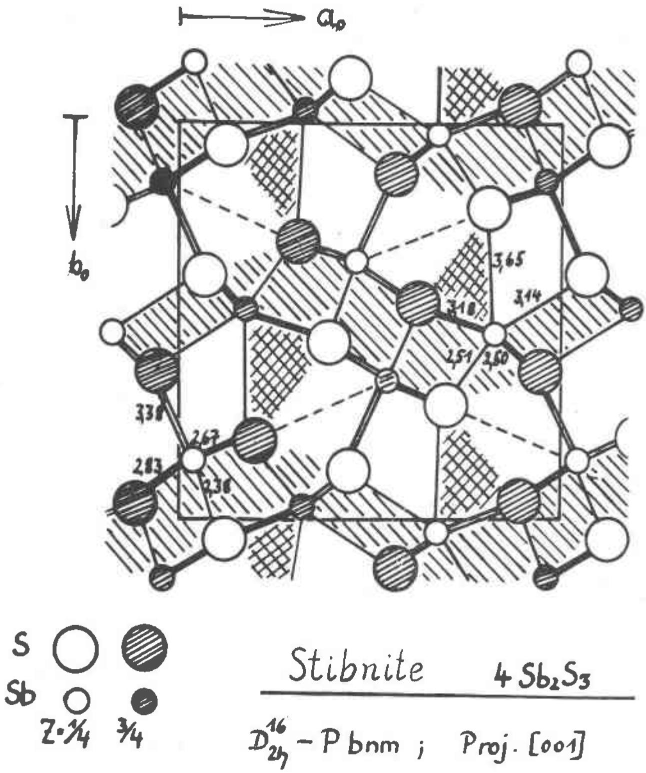

FIG. 4. Structure of stibnite projected on (001) indicating chains which are arranged in such a distorted way that the relations to the "net" structures are difficult to recognize.

If Sb constitutes the major part of the metal atoms, the ratio between metal and sulfide atoms becomes smaller and smaller until the limit, $f = n_{me}/n_s = 0.67$, is reached in stibnite. One third of the metal positions become unoccupied and the deformation of the octahedral holes reaches a maximum because the Sb atoms are strongly connected with only three sulfur atoms. Therefore the chains are small and irregularly arranged in respect to a changed galena type. Livingstonite (Niizeki and Buerger 1957*a*) also belongs in this group.

SUMMARY

The structures of the complex sulfides can be divided in two groups:

1) "Galena-like" structures have large portions with a distorted galena type (Fig. 2), with the coordination number 6 for most of the metal atoms; only the metal atoms on the edge of the galena parts

have another coordination number. Miargyrite, schapbachite, cosalite, meneghinite, the andorite group, galenobismutite, the krennerite, sylvanite and calaverite belong to this type.

2) The chain structure or "stibnite-like" structures are characterized by a high Sb (or Bi) content and by a change in their relation to the galena type indicated by the transformation from Fig. 2 to 3. The coordination number changes from 6 to 5+2 (=7); the chains have variable compositions and orientations to each other. The relation to Fig. 3 is shown by the structures of jamesonite and boulangerite; other sulfides with a chain structure but less closely related to Fig. 3 are livingstonite, stibnite, aikinite and wolfsbergite.

It seems reasonable to derive the "galena-like" complex sulfide structures from distorted three-dimensional lattice complexes, *i.e.* F-lattices, and the "stibnite-like" types from two-dimensional lattice complexes which indicate the chain character.

ACKNOWLEDGMENT

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