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# The Substructure of the Sulfosalt Jordanite \*)

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With 2 figures in the text

## Zusammenfassung

Die Substruktur von Jordanit,  $\text{Pb}_{26-28}\text{As}_{14}\text{S}_{46-48}$ , wurde ermittelt. Die Gitterkonstanten der wahren Struktur sind  $a_0 = 8,96 \pm 0,04$ ,  $b_0 = 31,92 \pm 0,01$ ,  $c_0 = 8,45 \pm 0,03 \text{ \AA}$ ,  $\beta = 117^\circ 50' \pm 10'$  und zeigen eine grosse Analogie mit den folgenden Perioden des PbS-Gitters:  $[110] = 8,40$ ,  $\frac{10}{3}[111] = 34,29$ ,  $[110] = 8,40$ ,  $\beta = 120^\circ$ ; die Raumgruppe  $C_{2h}^2-P 2_1/m$  wurde als richtig angenommen. Die Struktur, auf dem PbS-Gitter basierend, besteht aus einer  $2 \times 10 \times 2$ -Oktaederanordnung mit  $[111] \parallel b_0$ , denn es ist auch eine ausgesprochene Superperiode starker Reflexe mit  $h$  und  $l$  gleich gerade vorhanden. Die genaue chemische Zusammensetzung von Jordanit ist möglicherweise  $\text{Pb}_{26}\text{As}_{14}\text{S}_{46}$ . Die gefundene Substruktur gestattet eine zwangslose Erklärung der gesetzmässigen Verwachsung von Jordanit (010) mit Zinkblende (111).

## Summary

The substructure of jordanite,  $\text{Pb}_{26-28}\text{As}_{14}\text{S}_{46-48}$ , was deduced, using the similarity in the lattice dimensions with those of PbS:  $a_0 = 8.96 \pm 0.04$ ,  $b_0 = 31.92 \pm 0.01$ ,  $c_0 = 8.45 \pm 0.03 \text{ \AA}$ ,  $\beta = 117^\circ 50' \pm 50'$ — $[110]\text{PbS} = 8.40$ ,  $\frac{10}{3}[111] = 34.29$ ,  $[110] = 8.40$ ,  $\beta = 120^\circ$  and the superperiod of strong reflections with both  $h$  and  $l$  even; space group  $C_{2h}^2-P 2_1/m$ . The structure is based on a  $2 \times 10 \times 2$  array of octahedra with  $[111] \parallel b_0$ . The exact chemical composition possibly is  $\text{Pb}_{26}\text{As}_{14}\text{S}_{46}$ . The substructure explains the striking oriented overgrowths of jordanite (010) on (111) of sphalerite.

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## INTRODUCTION

The sulfosalt jordanite is one of at least ten intermediate phases which occur in the system  $\text{PbS-As}_2\text{S}_3$ . The mineral occurs near the PbS end of the series. Gratonite,  $\text{Pb}_9\text{As}_4\text{S}_{15}$ , is the only phase known which has a higher Pb : As ratio. The precise composition of jordanite has been the subject of much discussion [1] [2] [4] [6] [7] [8]. No completely satisfactory formula has yet been determined. The formulae which have been proposed may be summarized by the range of compositions  $\text{Pb}_{26-28}\text{As}_{14}\text{S}_{46-48}$ .

The present work is concerned with the substructure of jordanite: an average atomic arrangement over four closely related subcells. This does not permit specification of the precise chemical composition. A determination of the complete structure, however, is in progress, and will be reported in a subsequent communication.

## X-RAY INVESTIGATION AND COLLECTION OF INTENSITIES

Weissenberg patterns [3] showed jordanite to be monoclinic with the lattice constants listed in Table I. Systematic absences were observed for  $0k0$  reflections with  $k \neq 2n$ . This permits  $C_2^2 - P2_1$  and  $C_{2h}^2 - P2_1/m$  as possible space groups. Since the mineral is not piezoelectric [3] and possesses morphology of symmetry  $C_{2h} - 2/m$ ,  $C_{2h}^2 - 2_1/m$  has been selected as the probable space group.

Table I. *Comparison of the Lattice Constants of Jordanite with those of the PbS Structure*

<i>Jordanite</i>	<i>PbS</i> ( $a_0 = 5.94 \text{ \AA}$ )
$a_0 = 8.96 \pm 0.04 \text{ \AA}$	$[110] = 8.40 \text{ \AA}$
$b_0 = 31.92 \pm 0.01$	$\frac{10}{3} [111] = 34.29$
$c_0 = 8.45 \pm 0.03$	$[110] = 8.40$
$\beta = 117^\circ 50' \pm 10'$	$\beta = 120^\circ$

A complete three-dimensional set of diffracted intensities were obtained from a small spherical specimen, using  $\text{Cu } K_\alpha$  radiation. The intensities were recorded with an equi-inclination Weissenberg apparatus employing the multiple-film technique, and were measured with the aid of a double-beam recording microdensitometer. A total of 3973 independent reflections were detectable.

## SUBSTRUCTURE RELATIONSHIP

The cell dimensions of jordanite bear a fairly close relation to the PbS structure, as indicated in Table I. Diffraction patterns of jordanite display a marked superperiod of strong reflections with both  $h$  and  $l$  even. This corresponds to a substructure  $\mathbf{A}_0, \mathbf{B}_0, \mathbf{C}_0$  with

$$\begin{aligned}\mathbf{A}_0 &= \frac{1}{2} \mathbf{a}_0 = 4.48 \text{ \AA}, \\ \mathbf{B}_0 &= \mathbf{b}_0 = 31.92, \\ \mathbf{C}_0 &= \frac{1}{2} \mathbf{c}_0 = 4.22 \text{ (5)}.\end{aligned}$$

These relations strongly suggested that the structure was based on a  $2 \times 10 \times 2$  array of octahedra with  $[111]$  parallel to  $b_0$ .

## SOLUTION OF THE SUBSTRUCTURE

Three-dimensional Patterson functions were synthesized using all data and, in addition, using only the substructure reflections (i. e., those data with both  $h$  and  $l$  even). The complete Patterson function was essentially identical with four substructure Patterson cells, as was to be expected on the basis of the substructure relationship.

The high atomic number of the metal atoms in the structure cause the metal-metal interactions to be the strongest maxima in the Patterson function. The following features of the substructure Patterson function permitted location of the metal atoms:

1. Maxima occurred only at locations  $0y0$ ,  $\frac{1}{3}y\frac{2}{3}$ , and  $\frac{2}{3}y\frac{1}{3}$ . This required that the metal atoms have  $xz$  coordinates close to  $00$ ,  $\frac{1}{3}\frac{2}{3}$ , or  $\frac{2}{3}\frac{1}{3}$ .
2. Maxima occurred only at  $y$  coordinates of  $0, 0.1, 0.2, \dots$ . This required that the  $y$  coordinates of all metal atoms differ by multiples of  $0.1 b_0$ .
3. No maximum occurred at the location  $0\ 0.1\ 0$ . Metal atoms with  $y$  coordinates differing by  $0.1$  therefore could not have the same  $x$  and  $z$  coordinates. In other words, the metal atom polyhedra do not share faces in the stacking sequence along  $b$ .
4. Since the space group contains a symmetry plane at  $y = 1/4$ , the  $y$  coordinates of the metal atoms must be  $0.05, 0.15, 0.25, \dots$ , otherwise the polyhedra about metal atoms related by the symmetry plane would share faces.
5. Some of the maxima displayed a slight splitting along  $[201]$ . This indicated that the structure is distorted by a relative displacement of

the layers in this direction, and explained why  $a_0$  is appreciably larger than the value predicted by a regular array of octahedra.

These observations confirmed the supposition that the structure was based upon a  $2 \times 10 \times 2$  array of polyhedra, and reduced the determination of the metal atom positions to the problem of deducing a close-packed stacking sequence subject to the restrictions of the space group. Only 6 distinct sequences were found to be permissible. Of these, however, two possessed face-sharing of polyhedra and were discarded. Another possibility led to simple hexagonal close packing. Since this arrangement of metal atoms would predict an additional subperiod  $\mathbf{B}_0 = \frac{1}{5} \mathbf{b}_0$ , which is not observed, this model was accordingly discarded. Vector maps of the metal-metal interactions were computed for the remaining three models. An additional possibility could immediately be discarded on the basis of peak locations. The correct model was selected from the remaining pair on the basis of the relative weights of the maxima.

Least-squares refinement of the metal atoms locations, in which Pb was arbitrarily assigned to all metal atom sites, reduced  $R$  for 1049 reflections to 34.9%. Additional cycles of refinement, in which isotropic temperature factors and metal atom weights were varied, succeeded in reducing  $R$  to 30.4%. At this stage electron density and difference maps revealed three sites for sulfur atom locations. Further refinement including the sulfur atoms reduced  $R$  to 28.3% for the 1049 substructure reflections. The parameters obtained are listed in Table II.

Table II. *Atomic Positions and Temperature Factors for the Substructure of Jordanite*

Atom	x	y	z	B
M (1)	$0.360 \pm 0.002$	$0.0503 \pm 0.0002$	$0.687 \pm 0.002$	$1.41 \pm 0.10$
M (2)	$0.066 \pm 0.001$	$0.1479 \pm 0.0001$	$0.044 \pm 0.001$	$1.95 \pm 0.08$
M (3)	$0.718 \pm 0.003$	0.25	$0.371 \pm 0.003$	$0.91 \pm 0.16$
S (1)	0	0	0	$5.8 \pm 1.6$
S (2)	$0.800 \pm 0.016$	$0.093 \pm 0.002$	$0.395 \pm 0.016$	$5.4 \pm 1.1$
S (3)	$0.498 \pm 0.020$	$0.184 \pm 0.002$	$0.740 \pm 0.020$	$6.3 \pm 1.3$

#### DISCUSSION OF THE SUBSTRUCTURE

A projection of the asymmetric unit of the substructure on (010) is given in Fig. 1. The four subcells shown correspond to the average arrangement in the true structure. The layers are displaced along [201],

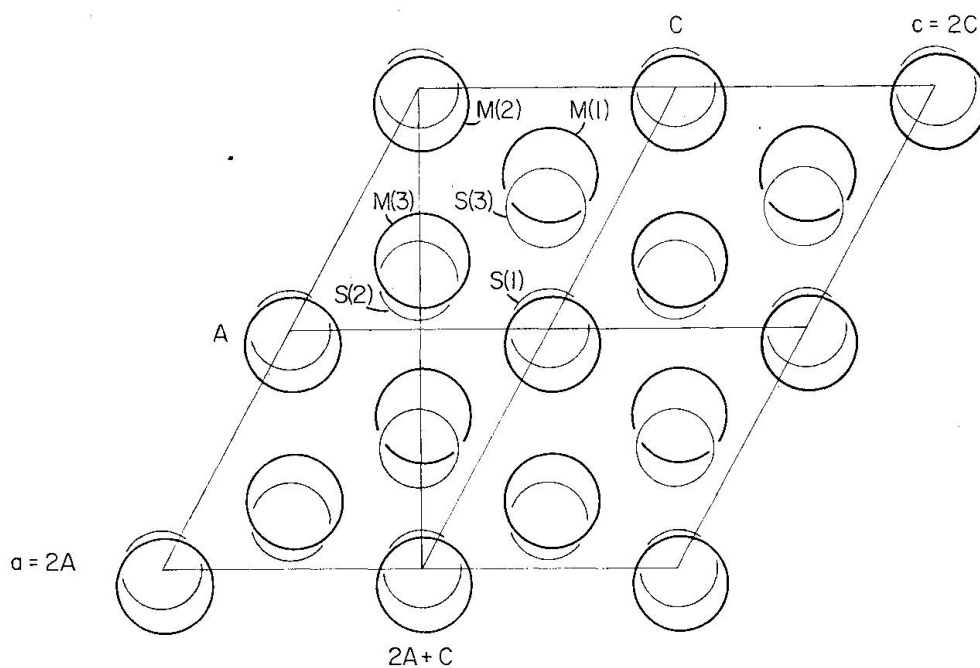


Fig. 1. Projection of the asymmetric unit of the jordanite substructure on (010). Four subcells, corresponding to the true structure, are indicated. Large circles represent metal atoms; small circles represent sulfur atoms.

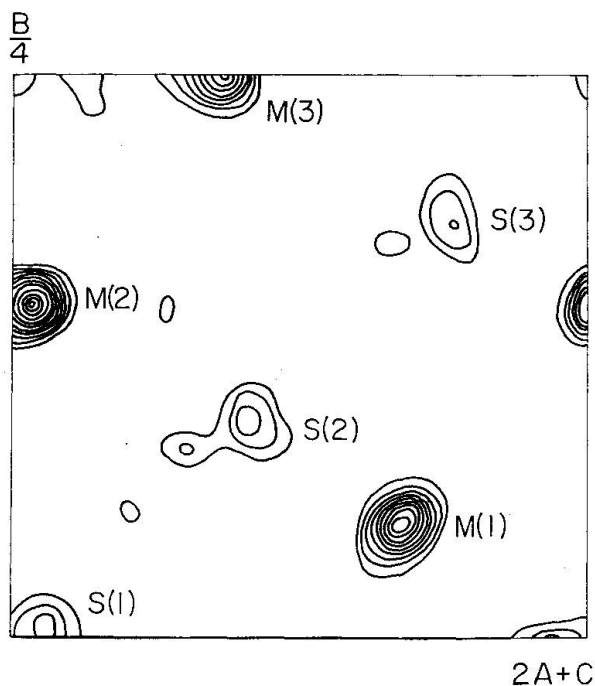


Fig. 2. Electron density section for the jordanite substructure. Contours at equal, but arbitrary intervals, zero contour omitted. Contour interval for metal atoms four times that of sulfur atoms. The section spans two unit cells and is indicated on Fig. 1 by a line.

but all atoms in the asymmetric unit lie close to  $(10\bar{2})$ , which is shown as a line in Fig. 1. The electron density in this section is given in Fig. 2.

The asymmetric unit of the substructure contains six atoms. A first metal atom, M (1), is octahedrally coordinated by six sulfur atoms at distances ranging from 2.61 to 3.09 Å. The average bond length for the six neighbors is 2.96 Å. The atom M (2) is in similar octahedral coordination with bond lengths ranging from 2.52 to 3.39 Å and averaging 2.95 Å. These average bond lengths are typical for Pb in 6-fold coordination. The atom M (3), however, has a loose trigonal prismatic coordination with bond lengths ranging from 3.05 to 3.74 Å and averaging 3.32 Å.

The stacking sequence within a unit cell is given by



where the upper case symbols denote metal atom sites, the lower case symbols denote sulfur sites and *A*, *B*, *C* refer to sites with *xz* coordinates 00,  $\frac{1}{3} \frac{2}{3}$ , and  $\frac{2}{3} \frac{1}{3}$ , respectively. The substructure thus consists of two PbS-like slabs, four octahedral units in thickness, rotated 180° about [111] with respect to one another. This rotation results in trigonal prismatic coordination for two of the ten layers of metal atoms in the cell.

As mentioned above, the metal atom weights were varied in the course of refinement in an attempt to determine the average Pb/As occupancy of each site. The substructure cell contains ten metal atoms and ten sulfur atoms, corresponding to  $M_{40}S_{40}$  in the true unit cell. It was therefore assumed that the unit cell contains  $Pb_{26}As_{14}$ . The best agreement with the ratio of metal atom weights obtained by least-squares refinement was obtained by assigning  $M(1) = 2 Pb + 2 As$ ,  $M(2) = 4 Pb$ , and  $M(3) = 1 Pb + 3 As$ . This suggests that the metal atom site with trigonal-prismatic coordination contains mainly As. This distribution, however, must remain tentative. A heavy atom considerably displaced from the average substructure position would contribute a smaller weight to the substructure intensities and thus give the illusion of a lighter atom occupying the site.

The composition given by the substructure still leaves a balance of 6 to 8 sulfur atoms to be located in the complement structure. It is interesting to speculate on the possible location of these atoms. In most arsenic sulfosalts based upon a PbS-like arrangement As has a loose 6-fold coordination, but has only three nearest neighbors. Arsenic atoms in the M (3) position can have this coordination only if a single short bond to S (3) occurs, and if an additional S atom is added in the symmetry plane. If M (3) indeed contains 3 As, as tentatively proposed, the

addition of 3 such additional S atoms to the complement structure would result in  $\text{Pb}_{26}\text{As}_{14}\text{S}_{46}$  as the correct composition of jordanite.

A difference map corresponding to Fig. 2 shows that the principal anomaly in the substructure at the present stage is a splitting of atoms, notably S (1) and M (3), into two locations. This effect is not unexpected in a substructure and represents the displacement of atoms present in the superstructure. The agreement between  $F_o$  and  $F_c$  for the substructure could have been further improved by the introduction of anisotropic temperature factors or split atoms. The present level of agreement, however, establishes the basic nature of the substructure and the additional work required to improve the disagreement index for the substructure reflections was more profitably devoted to the solution of the complement structure.

The close-packed nature of the substructure explains the striking oriented overgrowths of jordanite on (111) of sphalerite which have been observed in specimens from the Binnatal [5]. The structural model proposed is consistent with structural investigations of other Pb-As sulfosalts, which have indicated that phases near the Pb and of the series have structures based upon the PbS arrangement.

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The computations in this study were performed on several computers. The data reduction was performed on a Bull-Gamma Computer at the Institut für Angewandte Mathematik, Bern, for which we thank Professor W. Nef and Dr. R. Hüsler. A few cycles of refinement were performed on the IBM 1090 computer at C.E.R.N., Geneva, for which we thank IBM Extension Suisse and M. Héritier. The bulk of the computations were performed at the M.I.T. Computation Center.

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