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# ARSENOPYRITE CRYSTAL-CHEMICAL RELATIONS

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## ABSTRACT

The composition of naturally occurring arsenopyrite varies from about $FeAs_{0.9}S_{1.1}$ to $FeAs_{1.1}S_{0.9}$, as indicated by the more credible published chemical analyses and one new analysis. Analytical errors probably account for any apparent deviations of the Fe:(As+S) ratio from 1:2.

Five arsenopyrites of different compositions were studied by single-crystal $x$-ray methods. The changes caused by increasing arsenic content are (1) the triclinic symmetry approaches monoclinic, and (2) metrically the cell approaches the orthorhombic. These pseudosymmetries give rise to two types of twinning. Although refinements of the arsenopyrite crystal structure by means of ($h0l$) and ($hk0$) data were hampered by twinning, the atomic coordinates obtained in this investigation confirm those of Buerger (1936). The interatomic distances Fe-As, Fe-S, and As-S are 2.35, 2.25, and 2.33 Å, respectively.

Indexed $x$-ray powder data are given. The metrically monoclinic cell constants for six analyzed arsenopyrites relate linearly to arsenic content and inversely to sulfur content. Provided the combined minor element content is below 1%, the curve $d_{131}=1.6106+0.00098x$, where $x$ is the arsenopyrite arsenic content in atomic per cent, enables rapid determination of arsenopyrite compositions to within 1 atomic per cent.

## INTRODUCTION

Although arsenopyrite is relatively common in ore deposits, it has not received the careful attention often given to less common and economically less important minerals. A recent investigation of the phase relations in the Fe-As-S system (Clark, 1960) demonstrated that certain physical factors control the variation in composition of synthetic arsenopyrite. This warranted an examination of the compositional variations in naturally occurring arsenopyrite and a search for quantitative relations between composition and crystallographic properties.

Buerger's (1936, 1939) single-crystal $x$-ray investigations made a significant contribution to our knowledge of arsenopyrite symmetry and crystal structure. His work was hampered, however, by the use of twinned crystals, and the structure was finally derived by analogy with related structures. The importance of the mineral warranted a search for untwinned crystals, re-examination of the symmetry, and refinement of the structure.

Previously published $x$-ray powder diffraction data are entirely inadequate to explain the complexities in the powder pattern of arsenopyrite,

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and the available cell is of the wrong geometry for satisfactory indices to be calculated.

The present work on arsenopyrite symmetry, twinning, and crystal structure is the principal responsibility of Morimoto. For the most part Clark developed the discussions on arsenopyrite composition, indexing of *x*-ray powder data, and the composition-cell constant relation.

## PREVIOUS WORK

### *Arsenopyrite cell and symmetry*

The arsenopyrite cell was first determined by de Jong (1926) using the powder and rotation methods on arsenopyrite from Sulitjelma, Norway, which contained almost 7% cobalt. The orthorhombic crystallographic data were $a=6.45$, $b=9.54$, $c=5.53$ Å (from kX) and $Z=8$; the specific gravity was 6.28. The space group, determined from the indices of 17 powder reflections, was *Pmmm* or *Pmmn*.

Buerger (1936) studied arsenopyrite from Franklin, N. J., by the rotation and oscillation methods. The symmetry was orthorhombic with cell dimensions: $a=6.43$, $b=9.57$, and $c=5.72$ Å (from kX). In addition Buerger investigated arsenopyrite from the St. Peter Mine, Spindelmühle, Bohemia, by the Weissenberg method. Again the symmetry was orthorhombic, with cell dimensions of $a=6.43$, $b=9.53$, and $c=5.66$ Å (from kX). In both cases the possible space groups were *Cmmm*, *Cmm*2, and *C*222. Attempts to determine the arsenopyrite crystal structure on the basis of orthorhombic symmetry failed, and Buerger concluded that the symmetry was ideally monoclinic and commonly triclinic. By merely interchanging the axes mentioned above (we call it the first setting) by the transformation 001/100/010, Buerger adopted a conventional orientation of a monoclinic crystal (we call it the second setting). Thus, the respective space groups were $B2_1/d$ and $B\overline{1}$. Using the data obtained from twinned crystals, he determined the structure, by the trial and error method, as a derivative structure of marcasite, on the basis of space group $B2_1/d$. He attributed the deviation from monoclinic symmetry in "common" arsenopyrite to variations from the ideal chemical formula (FeAsS).

Huggins (1937) criticized the structures of marcasite and arsenopyrite, as determined by Buerger (1931, 1936), on the grounds that the structure led to interatomic distances not in harmony with those calculated from electron-pair bond radius sums. Buerger (1937) refined the structure of marcasite and confirmed its abnormal interatomic distances. For arsenopyrite, refinements were hampered by the difficulty of obtaining untwinned crystals; nevertheless, Buerger (1939) was able to suggest qualitative corrections to his published arsenopyrite parameters on the basis of the crystal structure of gudmundite (FeSbS) and confirmed that the interatomic distances in the arsenopyrite group are quite different from those derived from pyrite group minerals.

Incomplete powder patterns for natural arsenopyrite were published by de Jong (1926), Harcourt (1942), and Van Tassel (1954). Only de Jong's pattern was indexed, and that was on the basis of an orthorhombic cell.

### *Compositional variation of synthetic arsenopyrite*

The report of an earlier investigation (Clark, 1960) includes a résumé of previous experimental works pertinent to arsenopyrite, most of which were thermal decomposition studies. Clark found that the composition of arsenopyrite synthesized in sealed, evacuated tubes in the presence of equilibrium vapors varied as a function of temperature and that no one composition was stable throughout the temperature range of arsenopyrite stability. Arsenopyrites synthesized in the 630° to 660° C. range had the approximate composition $FeAs_{1.1}S_{0.9}$, whereas arsenopyrites richer in arsenic became stable at temperatures up to $702° \pm 3°$ C., the invariant temperature for the incongruent breakdown of arsenopyrite. Arsenopyrites richer in sulfur than is indicated by the theoretical composition FeAsS became stable only at temperatures below 450° to 500° C. The majority of natural arsenopyrites, as represented by published chemical analyses, lie in this sulfur-rich lower temperature range. Preliminary tests indicated that the composition and temperature limits of the sulfur-rich arsenopyrites were considerably extended by confining pressures of 2000 bars.

With various experiments Clark demonstrated that arsenopyrite, either natural or synthetic, would not equilibrate to new physical and chemical conditions even after months of heating at near-melting temperatures. Differences in the free energies of formation of arsenopyrites of different composition are very small.

Since arsenopyrites are frequently, perhaps universally, twinned, Clark explored for high-temperature crystallographic transitions, using differential thermal analysis with the samples in sealed, evacuated glass tubes. Neither natural nor synthetic arsenopyrite showed evidence of any transition from room temperature to 630° C.

## INDEXING OF POWDER PATTERNS

The powder diffraction patterns of some natural arsenopyrites show doubling of some of the major reflections, and the patterns are more complex in general than the published data would indicate (see, for example, pattern *a* in Fig. 1). The reflections cannot be indexed on the basis of an orthorhombic cell.

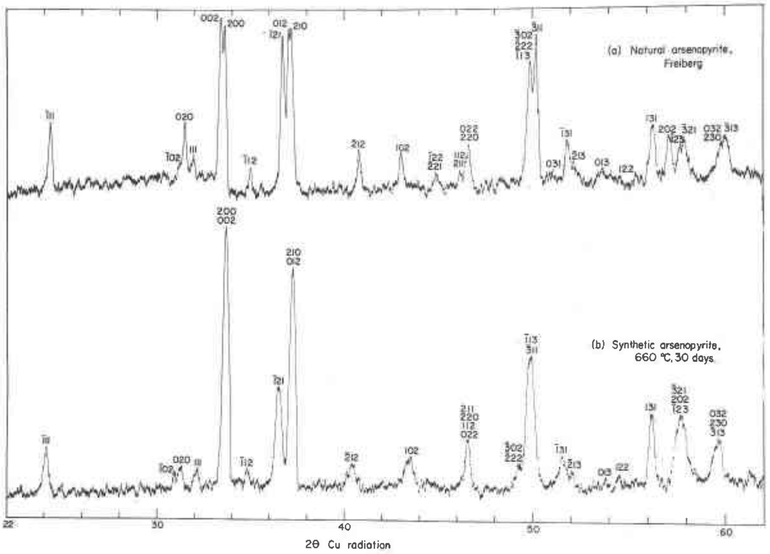

FIG. 1. Powder diffraction patterns of natural and synthetic arsenopyrites. They were obtained from smear-type mounts on a Norelco diffractometer with goniometer speed of one-half degree/minute. The intensity scale is linear.

A primitive monoclinic cell (we call it the third setting), derived from Buerger's (1936) double monoclinic, but metrically orthorhombic cell (the second setting) by transformation $\bar{\tfrac{1}{2}}0\tfrac{1}{2}/0\bar{1}0/\tfrac{1}{2}0\tfrac{1}{2}$, was employed as a first approximation in indexing the powder pattern.* The cell values were $a=c=5.76$, $b=5.66$ Å (from kX), $\beta=111°\ 47'$, with space group $P2_1/c$. Using arsenopyrite from Freiberg, Germany (Smithsonian Institution No. 103651), new primitive monoclinic cell dimensions were calculated from eight sets of measurements on the reflections $\bar{1}11$, 020, and the doublet 002,200. The improved cell values then facilitated revision of the initial indexing for the reflections that occur between 40° and 60° $2\theta$ (Cu radiation).

The powder diffraction patterns of all synthetic arsenopyrites are very similar. A typical one for arsenopyrite with a composition near $FeAs_{1.1}S_{0.9}$ is shown in Fig. 1*b*. The principal differences from the natural arsenopyrite pattern (Fig. 1*a*) are that the major peaks show no tendency to split and that the 202 reflection, which is isolated in natural arsenopyrite patterns, joins with the $\bar{3}21$ and $\bar{1}23$ reflections to form a single broad peak in synthetic arsenopyrite patterns. There are more subtle changes in the interplanar spacings of most of the other reflections. The pattern for

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* All crystallographic data and indices in the present paper are based on a primitive monoclinic cell (the third setting) unless otherwise indicated.

synthetic material could probably be indexed on a pseudo-orthorhombic cell, but the indexing based upon a primitive monoclinic cell is retained for ease of comparison. The variations in the powder patterns of natural and synthetic arsenopyrites are due to variations in the cell constants, which reflect compositional differences.

The arsenopyrite *x*-ray powder data are given in Table 1. The data for the Freiberg arsenopyrite are rather typical of natural arsenopyrites found in coexistence with pyrite or other sulfides from a sulfur-rich deposition environment. The synthetic arsenopyrite data more closely represent natural arsenopyrites grown in association with arsenide minerals such as loellingite ($FeAs_2$). There are all variations between, and slightly beyond, the limits of these sets of data. The observed spacings and intensities are averaged from two diffractometer patterns standardized with $CaF_2$. The values shown to five significant figures were determined more carefully for use in the least-squares calculation of the cell constants, which is discussed later. The cell constants for the Freiberg arsenopyrite are: $a=5.744\pm0.002$, $b=5.675\pm0.001$, $c=5.785\pm0.002$ Å, and $\beta=112.17°\pm0.02°$. Those for synthetic arsenopyrite are: $a=5.828\pm0.002$, $b=5.720\pm0.001$, $c=5.792\pm0.002$ Å, and $\beta=113.20°\pm0.02°$. The calculated spacings are based on these cells. Even excluding the absent reflections in space group $P2_1/c$, there are twice as many calculated reflections as are shown in Table 1. Using Weissenberg photographs of Freiberg arsenopyrite crystals, we were able to eliminate approximately 50% of the calculated reflections as being too weak to appear in a powder diffractometer pattern. For example, some of the higher angle peaks (Fig. 1) are assigned to three reflections. It was possible to omit as many as three other reflections because they made no significant contribution to the observed peak. Powder-camera films show, at *d* values below 1.5, five weak and several very weak reflections, which were not observed with the diffractometer, but show no additional reflections at higher *d* values.

## Composition of Natural Arsenopyrite

Sixteen published analyses, only two of which antedate 1928, are compiled in Table 2 to demonstrate the compositional variations of natural arsenopyrites. Analyses containing a few per cent cobalt, along with those which obviously have been performed on impure material, are not included. The sample location, the reference, the analyst, and, when available, pertinent information such as associated minerals and methods of purification and analysis, are listed.

It was hoped to supplement analysis No. 1, which represents carefully purified material from a sulfur-rich environment of deposition, with an

Table 1. *X*-Ray Powder Data for Natural Arsenopyrite from Freiberg, Germany, and Synthetic Arsenopyrite Grown in Coexistence with Arsenic and a Sulfur-Arsenic Liquid at 660° C.

CuKα radiation, λ = 1.5418 Å, Ni filter, Norelco diffractometer. Intensities taken proportional to the peak heights.

| Freiberg arsenopyrite | | | | Synthetic arsenopyrite | | | |
|---|---|---|---|---|---|---|---|
| *hkl* | *d* (obs.) | *d* (calc.) | I | *hkl* | *d* (obs.) | *d* (calc.) | I |
| $\bar{1}11$ | 3.6581* | 3.6576 | 40 | $\bar{1}11$ | 3.6970* | 3.6994 | 20 |
| $\bar{1}02$ | 2.866 | 2.866 | 5 | $\bar{1}02$ | 2.890 | 2.878 | 5 |
| 020 | 2.8382 | 2.8377 | 30 | 020 | 2.8632 | 2.8601 | 10 |
| 111 | 2.7963 | 2.7979 | 10 | 111 | 2.800 | 2.792 | 5 |
| 002 | 2.677 | 2.678 | 100 | 200 | 2.665 | 2.678 | 100 |
| 200 | 2.662 | 2.660 | 100 | 002 | | 2.662 | |
| $\bar{1}12$ | 2.557 | 2.558 | 10 | $\bar{1}12$ | 2.561 | 2.571 | 5 |
| $\bar{1}21$ | 2.4402 | 2.4405 | 90 | $\bar{1}21$ | 2.4645 | 2.4637 | 40 |
| 012 | 2.418 | 2.422 | 95 | 210 | 2.415 | 2.426 | 90 |
| 210 | 2.412 | 2.408 | 95 | 012 | | 2.413 | |
| $\bar{2}12$ | 2.2041 | 2.2040 | 25 | $\bar{2}12$ | 2.2330 | 2.2328 | 10 |
| 102 | 2.0955 | 2.0955 | 20 | 102 | 2.0797 | 2.0797 | 10 |
| $\bar{1}22$ | 2.017 | 2.016 | 5 | $\bar{2}21$ | 2.022 | 2.034 | 5 |
| $\bar{2}21$ | | 2.010 | | $\bar{1}22$ | | 2.029 | |
| 112 | 1.961 | 1.966 | 5 | 211 | 1.947 | 1.959 | 20 |
| 211 | | 1.960 | | 220 | | 1.955 | |
| 022 | 1.943 | 1.948 | 25 | 112 | | 1.954 | |
| 220 | | 1.941 | | 022 | | 1.949 | |
| $\bar{3}02$ | 1.824 | 1.830 | 70 | $\bar{3}02$ | 1.846 | 1.860 | 10 |
| $\bar{2}22$ | | 1.829 | | $\bar{2}22$ | | 1.850 | |
| $\bar{1}13$ | | 1.824 | | $\bar{3}11$ | 1.824 | 1.836 | 50 |
| $\bar{3}11$ | 1.814 | 1.812 | 90 | $\bar{1}13$ | | 1.826 | |
| 031 | 1.787 | 1.784 | 5 | 031 | | 1.795 | |
| $\bar{1}31$ | 1.7591 | 1.7592 | 20 | $\bar{1}31$ | 1.7741 | 1.7745 | 10 |
| $\bar{2}13$ | 1.750 | 1.748 | 5 | $\bar{2}13$ | 1.758 | 1.763 | 5 |
| 013 | 1.703 | 1.703 | 5 | 013 | | 1.695 | |
| 131 | 1.6307 | 1.6306 | 30 | 131 | 1.6378 | 1.6378 | 25 |
| 202 | 1.6080 | 1.6080 | 25 | $\bar{3}21$ | 1.597 | 1.605 | 25 |
| $\bar{1}23$ | 1.594 | 1.594 | 15 | 202 | | 1.599 | |
| $\bar{3}21$ | 1.589 | 1.586 | 20 | $\bar{1}23$ | | 1.598 | |
| 032 | 1.543 | 1.545 | 20 | $\bar{3}13$ | 1.555 | 1.556 | 15 |
| 230 | | 1.542 | | 230 | | 1.553 | |
| $\bar{3}13$ | 1.537 | 1.535 | 20 | 032 | | 1.550 | |
| $\bar{3}23$ | 1.390 | 1.390 | 5 | $\bar{3}23$ | | 1.407 | |
| $\bar{1}14$ | | 1.389 | | $\bar{2}14$ | | 1.396 | |
| $\bar{2}14$ | | 1.389 | | $\bar{1}14$ | | 1.388 | |
| 123 | 1.343 | 1.345 | 15 | 321 | 1.339 | 1.343 | 15 |
| 321 | | 1.340 | | 123 | | 1.339 | |
| 004 | | 1.339 | | 004 | | 1.331 | |

* Observed *d* values used in the least-squares calculation of cell constants are shown to four decimal places.

TABLE 2. RECENT ANALYSES OF ARSENOPYRITE IN WEIGHT PER CENT

| | FeAsS | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | 34.30 | 34.34 | 34.40 | 33.84 | 34.13 | 34.09 | 34.30 | 33.72 | 34.41 | 34.18 | 35.23 | 33.01 | 35.63 | 33.91 | 33.13 | 34.53 | 32.48 |
| Co | | 0.00 | <0.1 | ~0.3 | ~0.4 | — | — | — | 0.07 | 0.43 | — | — | — | trace | — | 0.09 | 1.16 |
| Ni | | 0.00 | ~0.03 | ~0.1 | ~0.03 | — | — | — | nil | 0.05 | — | — | — | — | — | — | — |
| Mn | | — | ≪0.03 | <0.03 | ≪0.03 | 0.004 | — | — | — | — | trace | — | — | trace | — | — | — |
| As | 46.01 | 44.33 | 43.82 | 44.45 | 44.00 | 43.82 | 43.64 | 46.52 | 42.28 | 42.37 | 41.77 | 49.91 | 43.03 | 45.10 | 45.83 | 44.34 | 48.72 |
| Bi | | 0.00 | — | — | — | — | — | — | 0.03 | — | — | — | — | — | — | 0.79 | — |
| Sb | | — | — | — | — | — | — | 1.44 | 0.18 | trace | 0.32 | — | — | — | — | — | — |
| S | 19.69 | 20.89 | 19.86 | 19.91 | 20.20 | 20.95 | 21.25 | 18.09 | 21.43 | 21.93 | 22.59 | 16.27 | 21.30 | 20.77 | 20.43 | 20.22 | 18.80 |
| Cu | | 0.15 | — | — | — | — | — | — | 0.04 | 0.78 | 0.15 | trace | — | — | — | — | — |
| Pb | | — | — | — | — | — | — | — | 0.22 | 0.24 | trace | — | trace | — | — | — | — |
| Zn | | — | — | — | — | — | — | — | — | — | 0.32 | — | trace | — | — | — | — |
| Insoluble | | 0.00 | — | — | — | 0.87 | — | — | 1.06 | 0.55 | 0.08 | 0.23 | 0.42 | — | 0.50 | — | ? |
| Total | 100.00 | 99.71 | 98.16 | 98.62 | 98.76 | 99.73 | 99.19 | 99.77 | 99.79* | 100.53 | 100.46 | 99.42 | 100.38 | 99.78 | 99.89 | 99.97 | 101.16 |
| S.G. | 6.18 | 6.08 | | | | 6.088 | | | 5.903 | | | | 5.67 | 6.01 | | | 6.199 |

ANALYSES RECALCULATED TO 100% SUBTRACTING: INSOLUBLE, Cu AS $CuFeS_2$, Pb AS PbS, AND Zn AS (Zn, Fe)S CONTAINING 7.5% Fe

| | FeAsS | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | 34.30 | 34.46 | 35.04 | 34.32 | 34.56 | 34.48 | 34.58 | 33.80 | 35.02† | 34.38 | 35.27 | 33.28 | 35.64 | 33.98 | 33.33 | 34.54 | 32.11 |
| Co | | 0.00 | <0.1 | ~0.3 | ~0.4 | — | — | — | 0.07 | 0.44 | — | — | — | trace | — | 0.09 | 1.15 |
| Ni | | 0.00 | ~0.03 | ~0.1 | ~0.03 | — | — | — | nil | 0.05 | — | — | — | — | — | — | — |
| Mn | | — | ≪0.03 | <0.03 | ≪0.03 | 0.004 | — | — | — | — | trace | — | — | trace | — | — | — |
| As | 46.01 | 44.65 | 44.64 | 45.07 | 44.55 | 44.32 | 44.00 | 46.63 | 43.02 | 43.48 | 42.02 | 50.32 | 43.05 | 45.20 | 46.11 | 44.35 | 48.16 |
| Bi | | 0.00 | — | — | — | — | — | — | 0.03 | — | — | — | — | — | — | 0.79 | — |
| Sb | | — | — | — | — | — | — | 1.44 | 0.06 | trace | 0.32 | — | — | — | — | — | — |
| S | 19.69 | 20.89 | 20.23 | 20.19 | 20.46 | 21.19 | 21.42 | 18.13 | 21.73<br>Se = 0.07 | 21.65 | 22.39 | 16.40 | 21.31 | 20.82 | 20.56 | 20.23 | 18.58 |

* Includes 0.07% Se.

† In analysis 8 the Pb and Cu were subtracted as a mixture of sulfosalts with an estimated average composition of Pb = 47, Sb = 26, Cu = 9, and S = 18%.

## Localities of Analyzed Arsenopyrites

1. Freiberg, Germany. (Smithsonian Institution, Washington, D. C., specimen No. 103651.) Clark, 1960. Asp* associated with py, cp, sp, and gn. Analysis performed by H. B. Wiik and P. Väänänen on $>1.5$ g of hand-picked material. S.G. is the mean of three measurements (6.13, 6.04, and 6.08) with a Berman balance.

2, 3, and 4. Brabant, Belgium. Van Tassel, 1954. Small asp crystals embedded in qtz veins in Cambrian phyllites. Some insoluble material was observed but was not recorded in per cent. It is supposed that inclusion of these insoluble fractions would bring the analysis totals nearer to 100%.

5. Nodatamagawa Mine, Iwate Prefecture, Japan. Kitahara, 1952. Prismatic crystals of arsenopyrite, together with qtz, filling fissure veins in country rock. Deposition presumably preceded the Mn, Fe, Pb, and Zn mineralizations. S.G. of 6.088 was calculated from the measured value of 6.008 by subtracting qtz.

6. Iname Mine, Aichi Prefecture, Japan. Yoshino, 1951. The mineral associations were not recorded. This analysis was performed by conventional means (As separated from Fe with $H_2S$ and determined by Volhard's method, Fe with $KMnO_4$, and S as $BaSO_4$) to check a new method of As determination using ion-exchange resin. The new technique gave similar results: Fe=34.13, As=43.89, S=21.11.

7. Varuträsk pegmatite, Sweden. Ödman, 1942. Analysis by Th. Berggren. Asp found in rock which may have been xenolith of amphibolite. Asp was microscopically homogeneous and no Sb mineral was observed.

8. Boliden Mine, Sweden. Ödman, 1941. Analysis by Th. Berggren. Asp in stubby, euhedral crystals up to 1 cm. These are cut by late veinlets, mostly of microscopic width containing a variety of Pb-Sb sulfosalts which probably account for most of the Pb and Sb in the analysis. There are many late minerals but py and cobaltite are the principal early associates of asp.

9. Felsöszalánk, com. Szepes, Hungary. Tokody, 1936. Analysis by G. Vavrinecz. Asp associated with tetrahedrite, cp, and qtz.

10. Kap-san, Kankyônandô, Korea. Tsurumi, 1934. Asp in 2–3 cm prismatic crystals cut by veinlets of cp. Asp crushed to $\sim$1 mm grains and hand picked. Tsurumi attributed the Cu in the analysis to cp. He stated that the method of As determination was not very good; this analysis was performed on the condensed vapor from asp heated at 700° C.

11. Ashio Mine, Totigi Prefecture, Japan. Okada, 1933. Asp associated with py, ms, cp, sp, and qtz. Okada indicated that the asp was difficult to purify—he hand picked asp with the aid of a microscope. He used Stokes' method for S and determined As as $As_2S_3$ which he believed gave a high value. Spectrographic analysis showed little other than Fe, As, and S.

12. Nogarè, Trentino, Italy. Andreatta, 1928*b*. Stubby asp crystals in veins with py, gn, sp, and qtz. The low S.G. is due to some siliceous impurities.

13. Calceranica, Trentino, Italy. Andreatta, 1928*a*. Asp in prismatic crystals from microscopic size up to 3 cm., which occur in talc mica schist adjoining mined pyrite vein.

14. Ronchi near Caldonazzo, Trentino, Italy. Andreatta, 1928*a*. Asp in crystalline masses with qtz in sericite and chlorite schists. Limonite prevalent and occasional pockets of py and sulfosalts.

15. O'Brien Mine, Cobalt, Ontario. Ellsworth, 1916. Asp as basal plates up to 2.5 mm in calcite and attached to arsenide masses. Both As and S were determined by fusion followed by titration of $Ag_3AsO_4$ or precipitation as $BaSO_4$.

16. Franklin Iron Company quarry, Franklin, New Jersey. Palache, 1910, 1935. Analysis by E. C. Sullivan. Asp crystals up to 1 inch long in limestone associated with py, po, spinel, humite, tourmaline, and phlogopite. The analysis was performed on 0.25 g. of material, and Sullivan noted that the As determination was probably too high and that silica and organic matter were also present.

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* Abbreviations of mineral names are in accordance with Chace (1956).

analysis of material from an arsenic-rich environment. Unfortunately, loellingite ($FeAs_2$) cannot be completely separated from arsenopyrite because they have very similar physical properties. The efficiency of a separation is difficult to estimate because the two minerals are almost indistinguishable optically, especially when the loellingite contains more than 1% sulfur in solid solution. Arsenopyrite coexisting with native arsenic is rare, and such material was unavailable. The only practical alternative was to use arsenopyrite that was not associated with either arsenide or sulfide minerals.

A specimen from Llallagua, Bolivia, obtained through the Smithsonian Institution (No. R-8069), contained stubby arsenopyrite crystals up to $\frac{1}{4}$ inch long occurring with minor amounts of quartz in what may have been a vug filling. One of the larger arsenopyrite crystals was fragmented and, upon microscopic examination of polished surfaces, was found to be completely homogeneous and free from other phases. After 90 seconds of etching with saturated $FeCl_3$ solution, no loellingite was detected. This material was chemically analyzed for Fe, Co, Ni, As, Bi, S, and Cu by Drs. H. B. Wiik and P. Väänänen, Helsinki, Finland. The results are given in Table 3.

To gain a visual comparison of the compositional variations recorded in Tables 2 and 3 the data have been plotted, in Fig. 2, on the expanded central portion of the Fe-As-S system. In plotting Fig. 2, Co, Ni, and Mn were included with Fe; Bi and Sb with As; and Se with S.

TABLE 3. ANALYSIS OF ARSENOPYRITE FROM LLALLAGUA, BOLIVIA, IN WEIGHT PER CENT

| Element | Content | Recalculated to 100% after subtracting $SiO_2$ |
|---|---|---|
| Fe | 33.01 | 33.05 |
| Co | 0.58 | 0.58 |
| Ni | 0.21 | 0.21 |
| As | 45.56 | 45.61 |
| Bi | 0.88 | 0.88 |
| S | 19.65 | 19.67 |
| Cu | <0.01 | |
| Insoluble | 0.04 | |
| | 99.93 | |
| Specific gravity* | 6.11 | |

* This is the mean of three determinations (6.16, 6.14, and 6.03) made with a Berman density balance.

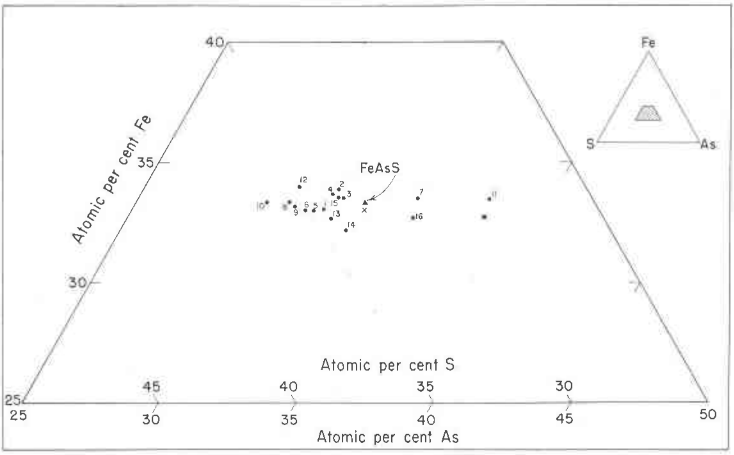

FIG. 2. Compositional variation of arsenopyrite shown on the central portion of the Fe-As-S diagram. The numbers correspond to specimen localities which are listed in the text. The cross represents the composition of arsenopyrite from Llallagua, Bolivia (Table 3); the solid square is an analyzed, synthetic arsenopyrite grown at 660° C.

The Bolivian analysis (shown by cross in Fig. 2) has equal proportions of arsenic and sulfur, as might have been expected from its environment. An arsenopyrite synthesized at 660° C. in the arsenopyrite-arsenic-liquid-vapor region (shown by solid square in Fig. 2) has a relatively high As:S ratio, with 4.64 atomic % more As than has the ideal FeAsS (Clark, 1960, Table 16). Only three of the natural materials have As:S ratios greater than unity, and for at least two of these (Nos. 11 and 16) the analyses are questionable. Arsenopyrite No. 11 occurred in a sulfur-rich environment! The analyst indicated that the sample was difficult to purify, and he believed the analyzed value for As was high. Analysis No. 16 was performed on only 0.25 g of material; this analyst also suspected that the As determination was high.

One analysis on material from Broken Hill, Australia, reported by Ramdohr (1950, p. 313) to be arsenic-rich arsenopyrite, has not been included in this compilation. On Fig. 2 it would fall beyond the limits of the diagram on the upper right-hand side, and on a phase diagram would plot in or near the pyrrhotite-loellingite two-phase region. Clearly, this analysis does not represent an arsenopyrite composition.

The majority of analyses in Fig. 2 are grouped on the high-sulfur side of the ideal FeAsS composition. Again some are more credible than others. With No. 10 the analyst suspected a poor As determination, and one of the older analyses, No. 15, was performed on arsenopyrite from an arsenic-rich environment. It should be noted that the composition of the

Freiberg arsenopyrite (No. 1), in which we have confidence, is 1.61 atomic % richer in sulfur than ideal FeAsS.

It is uncertain whether the variations of iron content, all within about ±0.6 atomic % of the mean value, truly represent different cation:anion ratios or reflect sampling and analytical errors. We believe that the differences represent errors, and that arsenopyrite does not vary measurably from the 1:2::cation:anion ratio* because three analyses by one analyst (Nos. 2, 3, and 4) are all iron rich, and three more by a different analyst (No. 1, cross, and solid square in Fig. 2) are all iron deficient by approximately the same amount. If these are errors they are consistent and may represent built-in biases in the two analytical procedures. (We do not know what procedures were used.) Three analyses (Nos. 12, 13, and 14) were performed by a third analyst and show the maximum and minimum iron contents of all the 18 analyses plotted in Fig. 2. Errors, if present in these last mentioned analyses, are random.

It is noteworthy that about 75% of the analyzed arsenopyrites have compositions richer in sulfur than ideal FeAsS. From experimental findings (Clark, 1960), it is clear that these arsenopyrites could only form at temperatures below 500° C.; however, this limit would be raised to about 650° C. under combined sulfur and arsenic activities equivalent to 2000 bars pressure. Arsenic-rich arsenopyrites could only form above about 300° to 400° C. The uneven distribution of analyses about ideal FeAsS relates principally to the frequence of suitable deposition environments, *i.e.* the predominance of sulfide-type over arsenide-type mineral deposits. Also, arsenopyrite when associated with arsenide minerals is much more difficult (if not impossible) to separate for chemical analysis than when it is associated with sulfides.

## VARIATION OF CELL DIMENSIONS AND $d_{131}$ WITH COMPOSITION

The composition of arsenopyrite is variable, and since this causes measurable changes in the *x*-ray powder diffraction patterns, it seemed desirable to determine the nature of the change in each of the four cell dimensions with changing composition. Only six chemically analyzed arsenopyrites were available for this part of the investigation; their source, composition, etc., were discussed earlier. These arsenopyrites were from Freiberg, Boliden, Nogaré, Calceranica (Table 2, Nos. 1, 8, 12, and 13), and Llallagua (Table 3), in addition to synthetic arsenopyrite grown at 660° C. in an arsenic-rich environment (Clark, 1960, Table 16).

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* Buerger (1936) postulated a small amount of proxy replacement of iron by arsenic in Franklin, N. J., arsenopyrite. This postulation was unwarranted because the cation deficiency is only 0.64 atomic %, and the analysis (No. 16, Table 2) is somewhat unreliable.

Theoretically, measurement of four appropriate reflections on the powder diffraction pattern would be sufficient to yield the four cell constants. However, the arsenopyrite pattern is not characterized by sharp reflections amenable to accurate measurement (see Fig. 1), and most of the strong peaks are due to two or more reflections. Therefore, it was decided to measure all the isolated reflections having reasonable definition and derive the best fitting cell by submitting the data to a least-squares calculation. The reflections measured were: $\bar{1}11$, 020, 111, $\bar{1}21$, $\bar{2}12$, 102, $\bar{1}31$, 131, and 202. (With the synthetic material, 111 and 202 were not measured.) The reflections were each measured in four diffractometer patterns obtained from two separate smear-type mounts with $CaF_2$ as internal standard ($a = 5.4626$ Å, Swanson and Tatge, 1953). The least-squares calculations were performed on the IBM 704 computer at the U. S. National Bureau of Standards, Washington, D. C.

In Fig. 3 the various cell constants are plotted as functions of the sulfur and arsenic contents. The sulfur and arsenic contents are shown to vary inversely. A plot of cell constants versus iron content of arsenopyrite gave a scatter of points. This was not surprising since Fig. 2 indicated very little variation in the iron content of 18 chemically analyzed arsenopyrites. The compositions are grouped in such a way as to place undue reliance upon the points representing the synthetic arsenopyrite; however, this composition is relatively well known. It should be noted that $h$ is equal to $l$ for all the reflections except 102. Therefore, the 102 reflection was the only one that differentiated between $a$ and $c$. Fortunately, relatively precise measurement of $d_{102}$ was possible. Using the cell constants so obtained, the differences between computed and observed $d$ values were almost always in the fourth decimal place as was shown in Table 1. In Fig. 3 the sizes of the data points are indicative of the precision. Larger errors are indicated for $a$ and $c$ than for $b$ and $\beta$. With respect to composition the points were arbitrarily given a width of $\pm 0.1\%$, which was, perhaps, too optimistic. Part of the scatter in the plotted points is due to fractional percentages of elements (other than Fe, As, and S) in solid solution. Through measurement of cell dimensions the composition of an arsenopyrite can be estimated. However, the result may not be reliable if the combined minor-element content exceeds 1 %.

The $d_{131}$ values for the various arsenopyrites are also shown in Fig. 3. In the previous investigation of the Fe-As-S system (Clark, 1960) the 131 interplanar spacing was used as a relative measure of arsenopyrite composition although the exact relationship was not established. This procedure was followed because the 131 spacing could be measured precisely and with relative ease, as compared with the time and labor required to derive the cell constants. Since the iron content never departs greatly from 33.3 atomic %, the curves shown here relate the 131 spacing quantitatively to the arsenopyrite composition. The sulfur and arsenic contents vary inversely indicating the mutual solid solution of these elements in arsenopyrite. Measurement of $d_{131}$ in a natural arsenopyrite will give the composition within 1%. The expression $d_{131}=1.6106+0.00098x$ relates

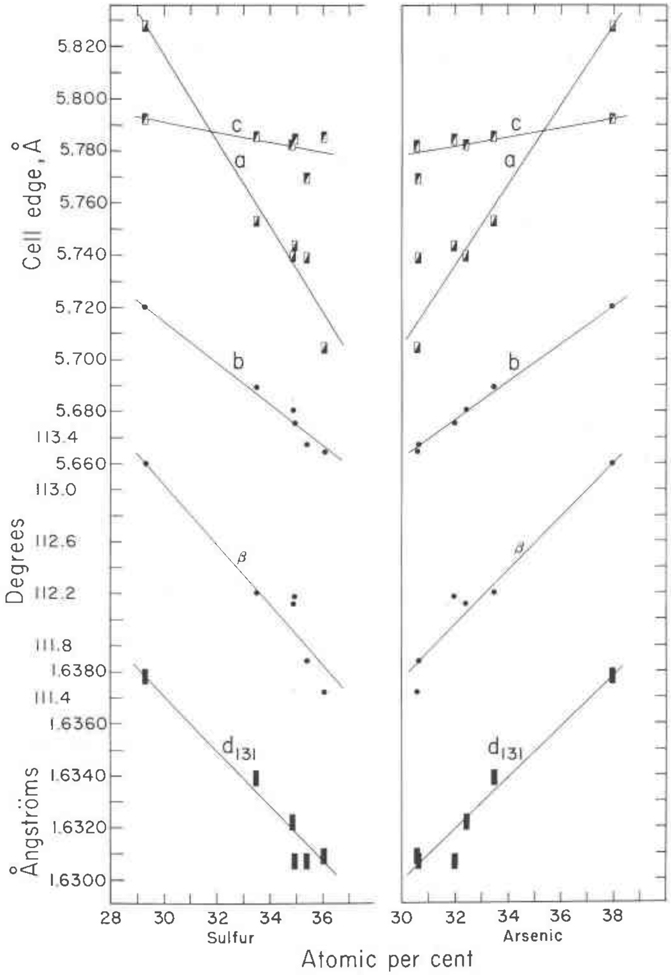

FIG. 3. Variations are shown in the arsenopyrite primitive monoclinic cell dimensions and $d_{131}$ values as functions of sulfur and arsenic content. The sizes of the data points represent the precision in the crystallographic quantities, but with respect to composition the points are arbitrarily estimated at ±0.1%. The arsenopyrite specimens used are: synthetic, Llallagua, Calceranica, Freiberg, Nogaré, and Boliden, in order of increasing sulfur content (decreasing arsenic content).

the arsenopyrite arsenic content ($x$) in atomic % to the $d_{131}$ value measured in angstroms.

## CRYSTAL STRUCTURE OF FREIBERG ARSENOPYRITE

The Weissenberg photographs of Freiberg arsenopyrite, taken by Mo radiation ($\lambda=0.71069$ Å), were used for the intensity data. The intensities were estimated visually and were corrected for the polarization and Lorentz factors. No absorption corrections were applied. The intensity data were placed on an absolute scale by comparing them with the calculated values.

Comparison of calculated and observed structure factors confirmed that Buerger's (1936) arsenopyrite structure is fundamentally correct. To explain the appearance of $h0l$ reflections with $l$ odd, in the Freiberg arsenopyrite, on the basis of Buerger's structure, we have to destroy the glide plane $c$ in $P2_1/c$ leaving the possible space groups $P2_1$ and $P\bar{1}$. It will be shown that arsenopyrite has triclinic symmetry; therefore, $P\bar{1}$ remains the only possible space group. Starting from Buerger's (1936) structure and adopting space group $P\bar{1}$, we obtained a structure which gave a residual, $R=\sum\left|\,|F_0|-|F_c|\,\right|/\sum|F_0|$, of 0.29 for 172 $h0l$ reflections and 0.20 for 135 $hk0$ reflections after four cycles of least-squares refinement. Using the final coordinates, the signs of $h0l$ and $hk0$ were determined and used in the calculation of electron-density projections on (010) and (001). Figure 4 shows the electron-density map on (010).

## ARSENOPYRITE SYMMETRY AND TWINNING

### *Freiberg arsenopyrite*

Crystals of Freiberg arsenopyrite were studied by the oscillation, precession, and Weissenberg methods using Fe, Cu, and Mo radiations. Of the ten specimens examined, all showed splitting of some reflections on the single-crystal photographs. In some instances this was merely a matter of slight randomness of orientation; however, most of the splittings were due to intrinsic properties of the crystals. In order to explain all the splittings, at least two types of twinning are required. The first type, described in detail by Buerger (1936) and referred to here as type-I twinning, has twin plane $(10\bar{1})$ or (101) or has twin axis $[10\bar{1}]$ or [101], respectively. The second type of twinning requires the assumption that arsenopyrite is triclinic; the postulated twin law is twin axis [010], which is equivalent to twin plane (010)*. We designate it type-II twinning. The deviations of $\alpha^*$ and $\gamma^*$ from 90° are less than 30′ and were not determined more closely.

Thus the Freiberg arsenopyrite has at least two types of twinning.

Type I results from the pseudo-orthorhombic symmetry of the lattice and type II from its pseudomonoclinic symmetry. Since the amount of type-I twinning, or volume ratio of the twin individuals, varies from specimen to specimen, it is supposed that this twinning takes place on a large scale, whereas type-II twinning occurs on a small scale, relative to the size of *x*-ray "single" crystals (~0.05 to 0.2 mm.). A photomicrograph, Fig. 5, shows the two types of twinning.

Triclinic symmetry of Freiberg arsenopyrite is most clearly revealed by the fact that the intensities of some ($hk0$) reflections are definitely different from those of the corresponding ($h\bar{k}0$) reflections. This justifies the existence of type-II twinning. Wilson's method (1949), applied on ($hk0$) reflections, confirmed the existence of a symmetry center. Thus, $P\bar{1}$ is the only possible space group.

Some crystals of Freiberg arsenopyrite were heated at 600° C. for 30 days in a sealed, evacuated, silica-glass tube and then rapidly cooled in cold water. Since the Weissenberg and precession photographs show no differences between the heated and unheated specimens, there is no evidence of a sluggish high-low polymorphic inversion.

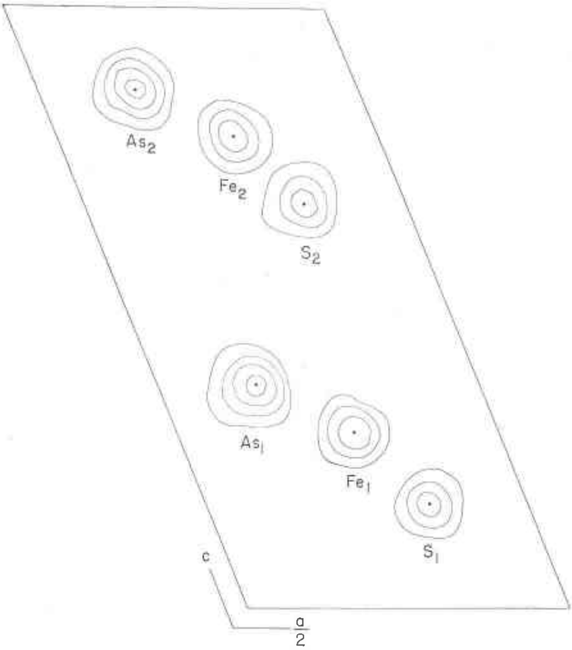

FIG. 4. Electron-density projection on (010). Contours are drawn at intervals of 11 $e/\text{Å}^2$ beginning at 10 $e/\text{Å}^2$.

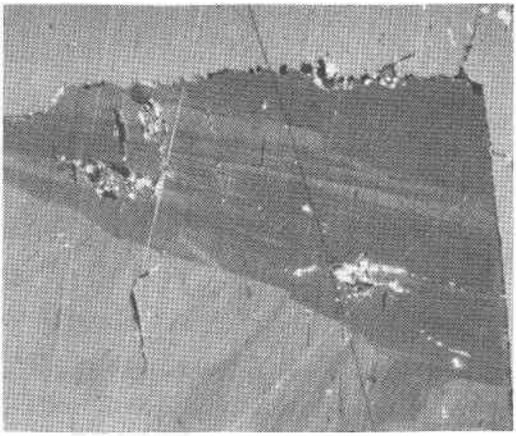

FIG. 5. In addition to the fine twinning of type II, the Freiberg arsenopyrite grain, which occupies about 90% of the photograph, also shows a type-I twin plane which divides it into two parts. White and black areas are pits. Taken with reflected light polarized in two directions.

### *Synthetic arsenopyrite*

Owing to the failure of experiments planned to synthesize crystals of the required size for use with the *x*-ray precession and Weissenberg cameras, only one synthetic arsenopyrite "single" crystal was examined.* The precession and Weissenberg photographs give orthorhombic symmetry, and the cell dimensions obtained from the precession photographs: $a=9.669$, $b=5.720$, and $c=6.400$ Å (all $\pm 0.005$). If the primitive monoclinic cell is employed for ease of comparison with the Freiberg arsenopyrite,† the above cell values transform to: $a=c=5.796$, $b=5.720\pm 0.005$ Å, and $\beta=113°\ 21'\pm 5'$. Using these values of $b$ and $\beta$ the composition of this synthetic arsenopyrite crystal is obtained from Fig. 3 as about 38 atomic per cent arsenic, or approximately $FeAs_{1.1}S_{0.9}$. The zero-level Weissenberg photograph of synthetic arsenopyrite about the $b$ axis, Fig. 6*b*, is compared with that of a Freiberg crystal, Fig. 6*a*. As fully discussed by Buerger (1936) in his investigation of arsenopyrite from Franklin,

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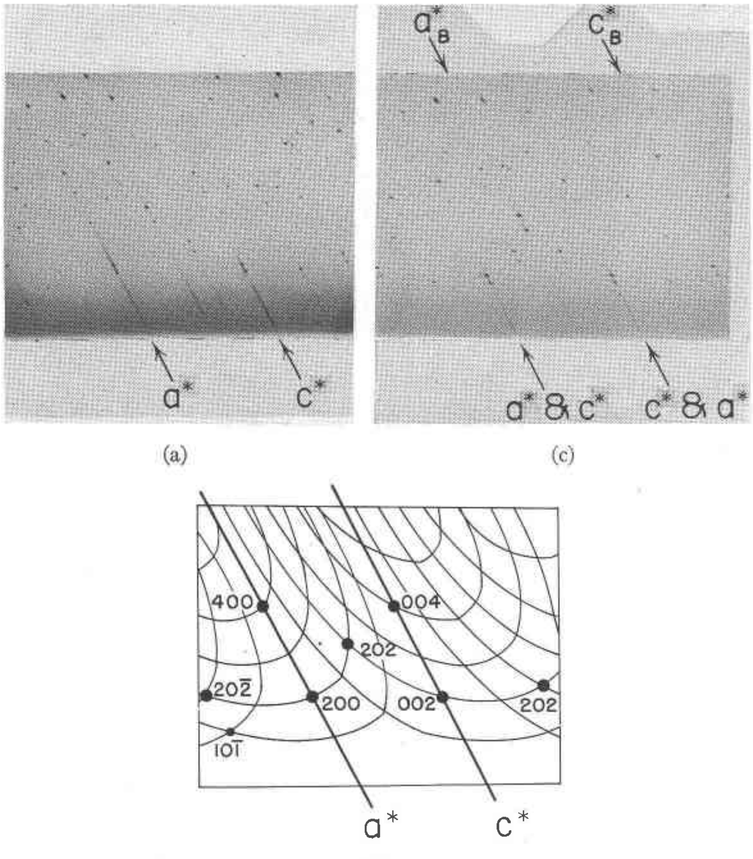
* Crystals of suitable size were grown under rather peculiar conditions of disequilibrium Arsenopyrite and arsenic were intergrown as an impervious mass at one end of a small, sealed tube at 600° C. This tube, open at the other end, was then heated for 3 days at 350° C. inside a larger sealed tube. A portion of the arsenopyrite decomposed to satisfy the vapor requirement of the large tube, and a 0.5 mm. layer of needle-shaped arsenopyrite crystals grew at the surface of the undecomposed arsenopyrite.

† The transformation from the pseudo-orthorhombic double cell (the second setting) to primitive monoclinic cell (the third setting) is given in the discussion of the powder pattern indices.

N. J., the apparent orthorhombic symmetry observed in the synthetic arsenopyrite is the result of type-I twinning of crystals of lower symmetry. Assuming space group $P2_1/c$, all the observed reflections but one can be explained by twinning. The one exception is $(10\bar{1})$, which proves that, although this synthetic arsenopyrite is nearly monoclinic, it really is triclinic, as fully discussed later.

*Effect of chemical composition*

Single-crystal investigations of the Freiberg and synthetic arsenopyrites show definite differences, not only in lattice constants, but also in



(a) (c)

(b)

Fig. 6. (Upper left) Zero level $b$-axis Weissenberg photograph of Freiberg arsenopyrite. (Upper right) Synthetic arsenopyrite. Apparent orthorhombic symmetry is clear where $a_B^*$ and $c_B^*$ represent Buerger's pseudo-orthorhombic axes. The intensities of $h0l$ with $l$ odd differ greatly. (Below) Diagram showing indexing of some reflections.

apparent symmetry. As previously discussed (see Fig. 2), these arsenopyrites differ in arsenic content by 6 atomic per cent. The composition of the Freiberg arsenopyrite lies on the sulfur-rich side of ideal FeAsS and appears to typify the majority of natural arsenopyrites, while that of the synthetic arsenopyrite is arsenic-rich relative to FeAsS and is near the limit of solid solution. It is reasonable to assume that these differences in the sulfur-to-arsenic ratio underlie the observed differences in reflection intensities and extinctions. To confirm this assumption, other specimens of natural arsenopyrite of known chemical compositions were studied using the Buerger precession method. The specimens are from (1) Llallagua, Bolivia; (2) New Consols Mine,* Cornwall; and (3) Boliden Mine, Sweden. The compositions and descriptions of these arsenopyrites are given in Tables 2 and 3. For the five specimens investigated the arsenic content decreases as follows: synthetic, New Consols, Llallagua, Freiberg, and Boliden.

The compositional variation in this series correlates with the following crystallographic observations:

(a) Crystals apparently free from type-I twinning† were found only in sulfur-rich arsenopyrite, i.e. in the Boliden and Freiberg specimens. These specimens show symmetry variations from pseudomonoclinic to pseudo-orthorhombic according to the relative volumes of the individuals in the twin. Type-I twinning was always observed for the Llallagua, New Consols, and synthetic specimens. The precession photographs for all the specimens from each of these three localities gave apparent orthorhombic symmetry without exception. Both types of twinning were observed in polished sections of some Freiberg specimens (see Fig. 5), but no twinning was observed microscopically in any of the other specimens. Our failure to observe this twinning microscopically is puzzling. Arsenopyrite anisotropic effects are small, and adjacent twin individuals may be so oriented as to show no visible difference. On precession and Weissenberg photographs of arsenic-rich "single" crystals, twinning is always visible. This implies that twinning occurs on a finer scale, so that it accounts for the more even volume distribution of the twin individuals in randomly selected specimens.

(b) The intensities of the $h0l$ reflections with $l$ odd decrease with increasing arsenic content. These reflections, clearly observed on the $x$-ray

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* Although a chemical analysis of the New Consols arsenopyrite is not available, its composition can be estimated from cell dimensions. Precession photographs give $b=5.718$ Å and $\beta=112.50°$. From $x$-ray powder data, $d_{131}=1.635$ Å. On Fig. 3 these values give mean compositions of 31 atomic % sulfur and 36% arsenic.

† The crystals may not be completely free from type-I twinning, but they give photographs like that shown in Fig. 6*a*.

photographs of Freiberg specimens, become weaker for specimens containing more arsenic, and are not observed in synthetic material except for the $(10\bar{1})$ reflection (see Fig. 6*c*). From the structural viewpoint the absence of these reflections indicates monoclinic symmetry. Therefore, the space group which is valid for sulfur-rich arsenopyrite specimens, namely $P\bar{1}$, approaches space group $P2_1/c$ with increasing arsenic content. Although none of the specimens examined had truly monoclinic symmetry, since the $(10\bar{1})$ was observed in all specimens, we presume that a crystal slightly more arsenic-rich than $FeAs_{1.1}S_{0.9}$ would have the space group $P2_1/c$. Thus, the replacement of sulfur by arsenic causes a gradual change in the arsenopyrite properties which raises the symmetry of the structure from triclinic to monoclinic.*

We can offer no reasonable theoretical explanation of these observations, which, it will be noted, do not fit the hypothesis of Buerger (1936), namely that arsenopyrite of the "ideal" composition FeAsS is monoclinic whereas compositional variations from the ideal render the symmetry triclinic. In view of the peculiar nature of the arsenopyrite stability field (Clark, 1960, Fig. 14), apparently the concept of any specific composition being "ideal" is invalid.

The electron-density maps give the following ratios of peak heights for the different atoms:

$$As:Fe:S::1.30:1.11:1.00$$

These peak heights require one of two assumptions: either the crystal used to collect the intensity data contains a small amount of type-I twinning, or there is 30% replacement of arsenic atoms by sulfur atoms and vice-versa. It has already been concluded that there is no appreciable substitution of iron for arsenic or sulfur. Comparisons were made between intensities of some strong $h0l$ reflections with $h$ odd and of their counter reflections $l0h$ in the supposed twin. The average ratio was 33:1. This is a direct measure of the relative volumes of the twin individuals if $h0l$'s were absent when $l$ is odd. However, some $h0l$'s with $l$ odd do appear; the volume contributed by the counterpart individual is thus even smaller than 1/33 of the total volume of the specimen.

When the volume difference between the twin individuals is so large, it is difficult to decide the relative effects of twinning and of the assumed partial sulfur-arsenic disorder on the intensity data. Both causes may be responsible, though twinning is probably the more important. This ambiguity renders further refinements of the structure impossible.

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* Rather than calling on further arsenic substitution, it is possible that the monoclinic structure may be attained by incorporation of minor amounts of elements such as cobalt or antimony in the arsenopyrite structure.

TABLE 4. ATOMIC COORDINATES IN ARSENOPYRITE
(in thousandths of cell edge)

| | Buerger, 1936 | | | Present study | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| As$_1$ | 147 | 372 | 353 | 154 | 371 | 363 |
| As$_2$ | (147 | 128 | 853)* | 155 | 129 | 863 |
| Fe$_1$ | 275 | 0 | 275 | 272 | 000 | 289 |
| Fe$_2$ | (275 | 500 | 775) | 275 | 502 | 787 |
| S$_1$ | 333 | −368 | 167 | 346 | −370 | 175 |
| S$_2$ | (333 | −132 | 667) | 343 | −131 | 675 |

* The coordinates given in parentheses are crystallographically equivalent to those immediately above.

The atomic coordinates adopted are those obtained in the first stage of the analysis without considering the effects on the intensities of either twinning or partial disorder. The *R* values for the coordinates are 0.29 for *h*0*l* and 0.21 for *hk*0. The coordinates are compared, in Table 4, with those given by Buerger (1936). The differences are slight. The accuracy of the coordinates cannot be estimated. Interatomic distances are calculated and given in Table 5. Average interatomic distances Fe-As, Fe-S, and As-S are 2.35, 2.25, and 2.33 Å, respectively. These values are in good agreement with those obtained for marcasite (Buerger, 1931) and loellingite (Buerger, 1932). Atomic radii derived from these interatomic distances are: $r(\mathrm{Fe}) = 1.14$, $r(\mathrm{As}) = 1.21$, and $r(\mathrm{S}) = 1.11$ Å. The structure is not accurate enough to warrant a discussion of the atomic distances, but it does support Buerger's (1936) arsenopyrite structure and atomic distances.

TABLE 5. INTERATOMIC DISTANCES IN ARSENOPYRITE
(in Ångströms)

| | | | | | |
|---|---|---|---|---|---|
| As$_1$–Fe$_1$ | 2.30 | S$_1$–Fe$_1$ | 2.29 | As$_1$–S$_1$ | 2.34 |
| –Fe$_2$ | 2.39 | –Fe$_2$ | 2.22 | As$_2$–S$_2$ | 2.33 |
| | 2.32 | | 2.25 | | |
| As$_2$–Fe$_1$ | 2.38 | S$_2$–Fe$_1$ | 2.24 | As –S | 2.33 |
| | 2.41 | | 2.26 | | |
| –Fe$_2$ | 2.32 | –Fe$_2$ | 2.26 | | |
| As –Fe | 2.35 | S –Fe | 2.25 | | |

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