The crystal structure of marrite, PbAgAsS₃

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Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday

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Auszug

Marrit aus dem Binnatal (Schweiz) der Zusammensetzung PbAgAsS₃ kristallisiert monoklin mit a = 7,2705, b = 12,6319, c = 5,9853 Å, $\beta = 91^{\circ}13,7'$, in der Raumgruppe $C_{2h}^5 - P2_1/a$. Die Struktur ist eine Überstruktur des PbS-Gitters. Sie wurde durch eine systematische Untersuchung aller möglichen Anordnungen, welche sich aus der Beziehung Sub-Superzelle ergaben, gefunden. Die Verfeinerung wurde bis zu $R = 10,9^{0}/_{0}$ getrieben, einem Wert, welcher durch die Zuverlässigkeit der Meßdaten gegeben war.

Die Struktur gleicht nur in sehr bedingter Weise der PbS-Struktur. As hat wie üblich drei nächste S-Nachbarn (2,26–2,28Å) in trigonal-pyramidaler Koordination. Ag weist drei nächste Nachbarn in Abständen zwischen 2,47 und 2,68Å bei fast ebener Anordnung auf. Ein viertes S-Atom befindet sich ungefähr normal zur Dreiecksebene im Abstande 2,91Å. Pb ist von sechs Schwefelatomen unregelmäßig-oktaedrisch (2,80–3,26Å) umgeben. Die S-Atome sind bis zu 1,09Å aus den idealen Substrukturlagen verschoben. Dies bedingt eine tetraedrische Koordination von zwei der drei S-Atome im asymmetrischen Fundamentalbereich.

Abstract

Marrite, a rare sulfosalt from the Binnatal, Switzerland, has been shown to have composition PbAgAsS₃. The phase is monoclinic, space group $P 2_1/a$, with a = 7.2705, b = 12.6319, c = 5.9853 Å, $\beta = 91^{\circ} 13.7'$. The structure is a superstructure based upon a PbS-like arrangement of atoms. The structure was solved through systematic consideration of all possible arrangements permitted by the subcell-supercell relationship. Refinement was carried to $R = 10.9^{\circ}/_{0}$, a value which was shown to represent a limit imposed by reliability of the data.

* Structural investigations of sulfides and sulfosalts, part 34; contribution No. 175 from the Abteilung für Kristallographie und Strukturlehre. The structure only superficially resembles the PbS arrangement. Arsenic has but three nearest S neighbors at distances between 2.26 and 2.28 Å, which together form the usual trigonal pyramid. Ag has three nearest neighbors between 2.47 and 2.68 Å with which it forms a group which is nearly planar. A fourth S atom is at an intermediate distance of 2.91 Å. Pb has six S neighbors at distances between 2.80 and 3.26 Å, which form an irregular octahedron. The S atoms are displaced by as much as 1.09 Å from the ideal substructure positions. This results in tetrahedral coordination for two of the three S atoms in the asymmetric unit.

Introduction

Marrite is an extremely rare sulfosalt known only from the Lengenbach quarry in the Binnatal, Canton Wallis, Switzerland. Fifteen small crystals were discovered by SOLLY (1905). Insufficient material was available to permit a chemical analysis, but the crystal morphology indicated that it was probably a new species. SOLLY (1906) later reported additional forms, but the mineral received no further study until recently (WUENSCH and NOWACKI, 1963).

At the time this work was begun, marrite was the only wellestablished phase which had not been rediscovered since the reopening (NOWACKI, 1960, 1963) of the Lengenbach¹. One of the original crystals obtained by SOLLY², approximately 1 mm in diameter, was kindly provided by Dr. G. F. CLARINGBULL. The present study was performed with two chips removed from this crystal.

Chemical composition

A chemical analysis of one fragment was performed at the Bureau de Recherches Géologiques et Minières, Paris, with the aid of electronmicroprobe fluorescence analysis. The analysis (WUENSCH and

	Microprobe analysis (WUENSCH and NOWACKI, 1963)	Ideal $PbAgAsS_3$
Pb	$41.0 \pm 1.0 ext{ wt }^{0}/_{0}$	42.62 wt ⁰ / ₀
Ag	23.7 ± 1.5	22.19
As	17.9 ± 0.5	15.41
s	18.8 ± 1.0	19.78
Σ	101.4	100.00

Table 1. Chemical composition of marrite

¹ Crystals of marrite were subsequently identified among specimens obtained from the Lengenbach during the summer of 1963 (NowACKI, et al., 1964).

² British Museum Catalogue No. 87130.

NOWACKI, 1963), Table 1, indicated that the phase had composition PbAgAsS₃. No other Pb—Ag arsenosulfide has yet been discovered.

X-ray examination

Precession photographs obtained from the second fragment indicated that the phase was monoclinic. Systematic absences were observed for h0l reflections with $h \neq 2n$ and for 0k0 reflections with $k \neq 2n$. The diffraction symbol is thus $2/mP 2_1/a$. This unambiguously specifies $P 2_1/a - C_{2k}^5$ as the correct space group.

Precise lattice constants were determined from back-reflection Weissenberg photographs (BUERGER, 1937). A least-squares extrapolation based on 29 0kl and 32 hol reflections, in which parameters characterizing systematic error due to film shrinkage, eccentricity and absorption were refined, was performed with the aid of the IBM 7094 program LCLSQ3 (BURNHAM, 1962). The lattice constants which were obtained, Table 2, confirm preliminary values obtained from precessison photographs (WUENSCH and No-WACKI, 1963), and are in excellent accord with the morphological data reported by SOLLY (1905). The density calculated for ideal PbAgAsS₃ is 5.876 g/cm³. Insufficient material was available for a density measurement with pycnometer techniques.

Table 2 further indicates that the lattice constants of marrite are

		Freieslebenite, PbAgSbS ₃ (Hellner, 1957)	7.53 Å	14.13	5.88	92°14′	0.5887:1:0.4597
ite and freieslebenite		Morphology (SOLLY, 1905)	l	I	l	91°15′	0.57634:1:0.47389
ole 2. Lattice constants of marri	Marrite, PbAgAsS ₃	Precession method (WUENSCH and NOWACKI, 1963)	$7.291\pm.008{ m \AA}$	∓ eo. ∏ coo.71	$5.998\pm.005$	$91^{\circ}13^{\prime}\pm2^{\prime}$	0.5748:1:0.4728
Tat		Precision lattice constants (present work)	$7.2705 \pm .0006 \text{\AA}$	1	$5.9853 \pm .0003$	$91^{\circ}13.7^{\prime}\pm0.2^{\prime}$	0.57557:1:0.47382
1			r a	0	υ	β	a:b:c

quite similar to those reported for freieslebenite, $PbAgSbS_3$ (HELLNER, 1957). Marrite appeared to be, perhaps, the As analogue of freieslebenite. A crystal-structure determination of marrite was undertaken to confirm the suspected isomorphism, and to permit comparison of the details of the two structures.

Substructure relationship

Diffraction patterns obtained from marrite indicated a marked superperiod of strong reflections when



Fig.1. Relation between the subcell and supercell of marrite

where p, q, and r are integers. This implied the presence of a facecentered pseudo-cubic subcell³ with $|A_1| = |A_2| = 5.5628$ Å, $|A_3| = 5.9853$ Å, $\alpha = \beta = 90^{\circ}48.1'$, $\gamma = 98^{\circ}23.3'$.

The relation between the true unit cell and subcell, Fig.1, is given by

$$\begin{aligned} \mathbf{a} &= \mathbf{A}_1 + \mathbf{A}_2 \\ \mathbf{b} &= -\frac{3}{2} \mathbf{A}_1 + \frac{3}{2} \mathbf{A}_2 \\ \mathbf{c} &= \mathbf{A}_2. \end{aligned}$$

³ Alternatively, a body-centered subcell (HELLNER, 1957) or primitive subcells may be defined, but this obscures the pseudo-cubic, PbS-like nature of the substructure.

The pseudo-cubic nature of the subcell and the similarity of its lattice constants to PbS (a = 5.96 Å) suggested that marrite was a superstructure based upon the PbS structure. A similar relation was deduced for freieslebenite by HELLNER (1957).

Intensity collection

The high linear-absorption coefficient of marrite ($\mu_l = 1033 \text{ cm}^{-1}$) necessitated an accurate correction for x-ray absorption by the specimen. The limited amount of material available precluded an attempt to grind a spherical specimen. The shape of the fragment of the crystal which had been removed for x-ray analysis, however, could be very satisfactorily approximated by a collection of six plane faces. This fragment, with overall dimensions $.103 \times .064 \times .064$ mm ($\mu_l r_{\text{max}} = 6.72$, $\mu_l r_{\text{min}} = 3.21$), was employed for the collection of intensities.

The intensities were recorded with an integrating equi-inclination Weissenberg camera employing the multiple-film method. The intensities were measured with the aid of a double-beam recording microdensitometer. Of the 1254 independent reflections contained within the CuK α sphere, a total of 1039 were measured. Many superstructure intensities were very weak, however, and only 804 reflections were detectable. Of these 99 were substructure reflections. This provided 13.2 observations per parameter in a subsequent least-squares refinement which employed anisotropic temperature-factor coefficients and separate scale factors for the individual levels. An attempt was made to measure each of the undetectable reflections. These were assigned magnitudes equal to one-half the minimum detectable value at that position on the film. Such values were usually determined by the level of background radiation recorded on the film.

The intensities were corrected for Lorentz and polarization factors with the aid of the program FINTE2 (ONKEN, 1964) appropriately modified to permit processing of data recorded on both the upper and lower portions of the films. Corrections for absorption were made with the program ACACA (WUENSCH and PREWITT, 1965).

Reliability of the data

The recorded intensities required a large correction for absorption effects. Several tests were therefore performed to assess the reliability of the final set of structure factors: (a) Measurement of a number of reflections was repeated to determine the reproducibility of the intensity measurement.

(b) Intensities on neighboring films in the pack were compared (following scaling of the smaller intensity by a film attenuation factor obtained by least-squares methods from all such pairs).

(c) Equivalent reflections on upper levels, and reflections related by Friedel symmetry on the zero-level were compared. This comparison provided a measure of any additional error introduced in the correction for absorption.

In each test the deviation from the mean value of $F_{\rm obs}$ was found to be a function of $F_{\rm obs}$, and increased as $F_{\rm obs}$ decreased (see Fig.3 below). The deviations on neighboring multiple films were independent of the level being recorded, but decreased slightly with the depth of the film pair in the pack due to a decrease in background intensity. The deviation from the mean value of $F_{\rm obs}$ for equivalent reflections decreased slightly for upper levels, presumably because of the decrease in the magnitude of the absorption correction required at higher diffraction angles.

Test	Number of observations	Average rms deviation from mean F_{obs}
Repeated measurement of same reflection	39	4.36º/0
Comparison of reflections on neighboring mul- tiple films	253	3.59º/ ₀
Comparison of equivalent reflections requiring different absorption corrections	200	10.40%

Table 3. Tests performed to assess reliability of set of structure factors

The results of these comparisons, summarized in Table 3, suggest that the accuracy of the intensity measurements limited the reliability of a typical structure factor to $\pm 4^{0}/_{0}$. An additional error of roughly $\pm 6^{0}/_{0}$ was introduced through error in the absorption correction.

The overall reliability of the entire set of measurable structure factors was estimated by first plotting the root-mean-square percentage deviation from the average structure factor of test (c) as a function, $\Delta(F)$, of the magnitude of these structure factors. The mean value of

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 Δ for the entire set of N observable structure factors was then obtained from

$$\bar{\varDelta} = rac{1}{N} \sum_{i=1}^{N} \varDelta(F_i) = 10.56 \, {}^0\!/_0 \, .$$

The value of a quantity analogous to the conventional disagreement index $R = \frac{\sum ||F_{\rm obs}| - |F_{\rm cal}||}{\sum F_{\rm obs}}$

defined by

$$r = \frac{\sum \overline{F_i} \Delta(\overline{F_i})}{\sum \overline{F_i}}$$

was found to be $8.97^{\circ}/_{\circ}$. It was subsequently found that the reliability of the data limited refinement of the structure to a comparable value of R.

Solution of the structure

It was assumed that marrite and freieslebenite might be isotypic. Refinement of a model based on that reported for freieslebenite (HELLNER, 1957), however, could not be carried to a value of R lower than $35^{\circ}/_{0}$. Attempts to interchange metal-atom locations or the position of the inversion center in the structure resulted in several models with comparable values of R (29 to $41^{\circ}/_{0}$) which could not be refined further. Electron-density and difference maps based on the structure-factor signs computed for these models were reasonable, but displayed slight anomalies of a sort which could not be removed by appropriate modification of the structure. It became apparent that a number of nearly homometric models existed, and that the true structure could be determined only through systematic consideration of all possible structures permitted by the substructure-superstructure relationship.

A Patterson function confirmed the PbS-like nature of the structure. The complement-structure Patterson function (that is, the Patterson function synthesized from the superstructure reflections alone) was too complex to be readily interpretable. This was due to fact that both the differences in metal-atom scattering power and displacements from the ideal substructure positions contributed significantly to the superstructure intensities.

The ideal metal and sulfur-atom positions were deduced from the PbS-like nature of the substructure in the following fashion. Certain inversion centers in an ideal PbS substructure must be suppressed in the formation of the superstructure. The inversion centers re-

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maining in an individual subcell must coincide with inversion centers in the true space group, and, furthermore, the placement of the subcell in the true unit cell must be such that the symmetry elements of the superstructure space group relate it to other subcells in the arrangement.

The PbS subcell has eight distinct inversion centers, each of which might be placed at an inversion center in space group $P2_1/a$ with $[110]_{PbS}$, $[\overline{1}10]_{PbS}$ and $[001]_{PbS}$ in the directions of a, b and c respectively. Of these possibilities, however, only two settings result in distinguishable PbS-like arrays in $P2_1/a$. For these choices the ideal metal-atom coordinates are



Fig.2. The two permissible settings of the PbS subcell. Large circles represent metal atoms at $z = \frac{1}{4}$. The small circles are inversion centers at z = 0

These models, Fig. 2, are related by a change of sign of the x coordinate. If β were exactly 90° the models would be homometric; since β differs only slightly from 90° they are nearly homometric.

Determination of the correct configuration was achieved by systematic examination of all possible metal-atom distributions in the two sets of ideal metal-atom positions. Structure-factor calculation and least-squares refinement were performed with the aid of the fullmatrix least-squares program SFLSQ3 (PREWITT, 1962). Neutral-atom form factors given by THOMAS *et al.*, POTTERS, FREEMAN and WATSON, and DAWSON were employed for Pb, Ag, As and S, respectively⁴. Corrections for anomalous scattering were made for all atoms.

The agreement between $F_{\rm obs}$ and $F_{\rm cal}$ for the substructure reflections was quite insensitive to the details of the model assumed. Only the superstructure reflections were therefore included in the initial computations. Further, since the difference between the metal-atom scattering power and the average substructure metal-position scattering power ($\Delta Z = +28, -7, \text{ and } -21$ electrons for Pb, Ag and As respectively) was comparable to the *total* scattering power of S, it was assumed that the distribution of the metal atoms would determine the majority of the superstructure-reflection signs. The metal atoms alone were therefore employed in the initial computations.

A total of six metal-atom distributions are possible for each of the two settings of the PbS substructure.

Consideration of Fig.2, however, shows that interchange of the metal atoms occupying the M(1) and M(2) positions is equivalent to a shift of the origin of the structure by $\frac{1}{2}00$. This reduced the number of models to be considered to six (in which As, Ag or Pb occupied the M(3) position in each of the two substructure settings⁵).

Beginning with the ideal metal-atom substructure positions, and with arbitrarily selected isotropic temperature factors of 1.0 Å², metal-atom positions and scale factors were varied to convergence for each of the six models. The additional substructure reflections were then included in the computation, and the S-atom locations determined with the aid of electron-density and difference maps. The sulfur atoms were then added to the refinement, and scale factors

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⁴ International tables for x-ray crystallography, Vol. III. Kynoch Press, Birmingham (1962), 201-212.

⁵ The magnitudes of the Patterson-function maxima precluded placement of Pb in the M(3) position, but this model was also examined in the interests of completing Table 4.

Assignment of		Setting 1			Setting 2	
atoms to $M(1)$, M(2), M(3)	PbAgAs AgPbAs	PbAsAg ^a AsPbAg	AgAsPb AsAgPb	$egin{array}{c} { m PbAgAs^b} \ { m AgPbAs} \end{array}$	PbAsAg AsPbAg	AgAsPb AsAgPb
Metals only, superstructure reflections only; scale factors and positions varied	28.3º/₀	27.7º/₀	40.3º/₀	31.7%/0	31.9%/0	36.0º/ ₀
Metals only, all reflections; scale factors varied	26.4	25.4	41.1	35.7	54.8	38.6
Sulfur atoms added; scale factors varied	19.1	17.1	46.6	35.9	53.7	44.1
All atoms, all reflections; scale factors and positions varied (equal weights)	16.8	15.5	40.7	25.9	31.9	37.2

Table 4. Comparison of refinements of possible models for the structure of marrite

^a Correct structure for marrite.

^b Model proposed for freieslebenite (HELLNER, 1957).

and positions again varied to convergence. It is of interest to note that most of these models could be refined to respectable values of R. The details of this procedure are summarized in Table 4. One of the models afforded far better agreement between observed and calculated structure factors, and this arrangement was selected as the correct structure. This model was subsequently refined to the limits imposed by the reliability of the data, which further confirmed the correctness of this choice.

Refinement of the structure

Additional cycles of least-squares refinement in which all observable reflections were equally weighted, and in which isotropic temperature factors were varied reduced R to $14.8^{\circ}/_{\circ}$. At this point R was evaluated as function of F_{obs} . The weighting scheme adopted in subsequent cycles was chosen such that the product of weight and R was independent of F_{obs} . Additional cycles of refinement with this weighting scheme reduced R to $12.8^{\circ}/_{\circ}$.

Electron-density and difference maps indicated no anomalies other than an indication of slight anisotropic thermal motion. Complete correlation between the scale factors for the individual levels and the temperature-factor coefficient β_{11} was to be expected if anisotropic refinement was attempted (LINGAFELTER and DONOHUE, 1966). To minimize this effect, the scale factors obtained in the final cycle of isotropic refinement were used to reduce all $F_{\rm obs}$ to the same scale. Several additional cycles of refinement were then performed in which the single scale factor and positions, and anisotropic temperature-factor coefficients were alternately varied to convergence. A final cycle of refinement was then performed in which individual scale factors were again varied.

The final value of R for 804 observed structure factors was $10.9^{0}/_{0}$. The weighted root-mean-square R, $[\Sigma w(|F_{obs}| - |F_{cal}|)^{2}/\Sigma wF^{2}_{obs}]^{\frac{1}{2}}$, was $11.8^{0}/_{0}$. When the 235 undetectable structure factors were included in the computation at one-half the minimum observable value, R was $12.8^{0}/_{0}$.

The value of R was found to increase sharply as $F_{\rm obs}$ approached the minimum observable value. Figure 3 presents a plot of R, evaluated for groups of 20 structure factors to reduce scatter, as a function of the magnitude of the average structure factor in the group. Figure 3



Fig. 3. Variation of R with the magnitude of F_{obs} (open circles), compared with the variation of an analogous quantity, r, based on comparison of equivalent structure factors (solid circles)

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further shows that this dependence closely matches the variation of r (defined above), obtained from measurements of equivalent F_{obs} . The curve asymptotically approaches a value of $6^{0}/_{0}$, which was estimated to be the uncertainty in the correction for absorption. The disagreement in excess of $6^{0}/_{0}$ was found to vary linearly with $1/F_{obs}$. This suggests the introduction of an error in each F_{obs} which is independent of the magnitude of the structure factor. Conversion of this error to units of intensity showed that it could be satisfactorily accounted for by uncertainty in the assignment of background level in the densitometer traces.

Atom	Parameter	Displacement from ideal substructure position	Magnitude of displacement
As	$x = .3557 \pm .0008$ $y = .0906 \pm .0005$ $z = .2786 \pm .0009$ $B = 0.92 \pm .09$ Å ²	0193 + .0073 + .0286	$0.242 \pm .006$ Å
Pb	$egin{array}{rl} x &=& .3383 \pm .0003 \ y &=& .4111 \pm .0002 \ z &=& .2521 \pm .0004 \ B &=& 1.11 \pm .03 \ { m \AA}^2 \end{array}$	0367 0056 +.0021	$0.276\pm.002$
Ag	$egin{array}{rl} x=&.3882\pm.0008\ y=&.7633\pm.0005\ z=&.1851\pm.0009\ B=2.31&\pm.10\ { m \AA}^2 \end{array}$	+.0132 +.01330649	$0.436\pm.005$
S(1)	$egin{array}{rl} x &=& .1460 \pm .0020 \ y &=& .2145 \pm .0010 \ z &=& .3817 \pm .0022 \ B &=& 1.11 & \pm .22 \ { m \AA}^2 \end{array}$	$+.0210 \\0355 \\ +.1317$	$0.917 \pm .013$
S(2)	$x = .1528 \pm .0018$ $y = .6230 \pm .0011$ $z = .0926 \pm .0020$ $B = 0.91 \pm .21$ Å ²	+.0278 +.03971574	$1.089\pm.013$
S (3)	$\begin{array}{l} x = .1658 \pm .0020 \\ y = .9481 \pm .0011 \\ z = .2870 \pm .0020 \\ B = 1.06 \pm .22 \text{ Å}^2 \end{array}$	+.0408 + .0314 + .0370	0.541 ± .014

Table 5. Atom locations and isotropic temperature jactors* for marrite

* Following completion of isotropic refinement, $R = 12.8^{\circ}/_{0}$.

The crystal structure of marrite

Atom	βιι	Equivalent isotropic temperature factor
As	$egin{array}{rll} eta_{11} = & .0084 \pm .0013 \ eta_{22} = & .0006 \pm .0003 \ eta_{33} = & .0047 \pm .0014 \ eta_{12} =0005 \pm .0005 \ eta_{23} = & .0007 \pm .0006 \ eta_{31} = & .0016 \pm .0008 \end{array}$	0.87 Å
Ръ	$egin{array}{rll} eta_{11} = & .0032 \pm .0005 \ eta_{22} = & .0022 \pm .0001 \ eta_{33} = & .0095 \pm .0005 \ eta_{12} = & .0000 \pm .0002 \ eta_{23} = & .0004 \pm .0003 \ eta_{31} = & .0016 \pm .0003 \end{array}$	1.09
Ag	$egin{array}{rll} eta_{11} = & .0131 \pm .0014 \ eta_{22} = & .0041 \pm .0004 \ eta_{33} = & .0153 \pm .0015 \ eta_{12} =0035 \pm .0005 \ eta_{23} = & .0006 \pm .0005 \ eta_{31} = & .0039 \pm .0010 \end{array}$	2.36
5(1)	$\begin{array}{rcl} \beta_{11} = & .0079 \pm .0035 \\ \beta_{22} = & .0010 \pm .0008 \\ \beta_{33} = & .0108 \pm .0036 \\ \beta_{12} =0006 \pm .0010 \\ \beta_{23} =0011 \pm .0014 \\ \beta_{31} = & .0036 \pm .0022 \end{array}$	1.13
5(2)	$\begin{array}{rcl} \beta_{11} = & .0027 \pm .0031 \\ \beta_{22} = & .0025 \pm .0008 \\ \beta_{33} = & .0079 \pm .0032 \\ \beta_{12} = & .0001 \pm .0010 \\ \beta_{23} =0017 \pm .0012 \\ \beta_{31} = & .0021 \pm .0019 \end{array}$	1.01
S(3)	$\begin{array}{rrrr} \beta_{11} = & .0138 \pm .0036 \\ \beta_{22} = & .0009 \pm .0007 \\ \beta_{33} = & .0061 \pm .0036 \\ \beta_{12} =0003 \pm .0011 \\ \beta_{23} = & .0000 \pm .0012 \\ \beta_{31} = & .0034 \pm .0023 \end{array}$	1.32

Table 6. Anisotropic temperature-factor coefficients

Table 7. Comparison of observed and calculated structure factors

ь	k	1	S . P	P	ь	Ŀ	1	8 . F	P		Ŀ	,	e . P	υ.			. 1		-
		÷.	"h obs	"cal		•	1	h'obs	fcal	4			"h' obs	cal			K T	b. obs	cal
0	0	2	443.3	476.9	1	1 .	-4	101.4	93.3	1	8	-5	36.6	69.9	2		2 -4	144.4	140.4
		3.	30.8	18.9			-3	76.6	70.1			-4 *	22.1	48.0			-3	* 41.7	40.8
		4	224.0	204.0			-2	150.2	147.2			-3	113.7	120.0			-2	238.7	215.8
		5	28.3	27.3			-1	93.1	114.4			-2	77.8	84.1			-1	* 17.8	18.9
		2	157.3	136.2			0	53.1	71.7			-1	149.4	152.5			0	-86.4	94.4
•		6	22.2	100 5			1	59.0	03.3				91.0	91.6			1	36.7	1.5
		÷	100 1	199.9			-	61.0	23.7			1	59.5	03.1			2	32.5	43.0
		ί.	110.1	05 4			2	70 5	70.0			2 .	121.0	122.0			?	- 28.0	28.7
		-	116 0	112 7			2	105.2	J9+9 D7 0			2	110 5	23.3			4	67.1	29.9
		6	26.7	33.5			6 .	18.3	10.5			÷ *	17.9	17.8			6	20.0	9.0
		7	100.7	101.9			7	52.8	72.2			6	74.2	79.2			7	76 1	04 3
0	2	i i	52.2	47.5	1	2 .	-ż	40.1	50.4	1	9	-6	20.4	13.1	2		3 -7	64.1	83.6
		2	94.9	89.3			-6 *	28.1	23.0			-5 *	24.3	28.7			-6	109.6	97.8
		3	143.4	128.2			-5	68.8	79.4			_4 *	20.8	41.1			-5	77.8	91.9
		4	161.5	148.6			-4	111.1	105.2			-3	52.4	50.9			-4	196.1	161.1
		5	139.0	126.1			-3	46.8	56.5			-2 *	29.6	14.9			-3	89.3	82.1
		6	108.9	104.2			-2	141.8	125.4			-1 *	23.9	37.0			-2	340.2	356.7
		7	51.5	55.8			-1	95.3	87.2			0*	29.0	40.6			-1	73.9	54.6
0	3	1	392.3	418.8			0	86.3	120.1			1*	23.5	22.8			0	370.9	556.6
		2	79.8	76.0			1	104.7	107.0			2	46.5	34.4			1	121.2	105.8
		2	343.0	50.8			2.	212.5	213.5			2 *	20.8	4.9			2	442.1	380.2
		4	167 0	29.9			2.	25.9	9.8			2	/5.0	62.8			- ?	159.9	114.3
		6.	107.2	17.0			2.	191.7	100.0		••		29.5	44.7			-	247.4	181.8
		7	50 7	51 9			6	62.9	85 1	1	10	-? ÷	14.0	24 7			2	51.1	51.8
0	4	ò	112.8	91.8			ž	30.2	42.4				20.8	5.6			7	+ 7 4	0.6
-	-	1 *	17.4	5.7	1	3.	-ż *	15.5	10.1			-2 *	29.7	42.6	2		k -7	68.5	87.7
		2	99.2	92.0	-	÷.,	-6 *	23.7	19.7			-1 *	23.4	32.8	-		-6	87.4	82.5
		3	110.9	99.1			-5 *	24.1	12.1			0	54.0	61.0			-5	123.3	108.7
		4	145.8	137.1			-4 *	37.3	39.0			1 *	26.3	17.1			-4	151.0	140.3
		5	136.0	119.4			-3 *	22.3	28.2			2*	26.3	6.7			-3	178.8	154.2
		6	143.8	138.5			-2 *	25.3	5.2			3	58.0	63.4			-2	256.8	236.9
	-	7.	18.4	29.0			-1	50.4	44.3		• ·	5	51.8	49.2			-1	113.1	106.3
0	5	1 *	18.9	15.2			0	32.7	37.4	1	11	-5 *	11.3	12.4			0	102.0	107.0
		2	03.0	00.2			1	23.3	25.2			-4	37.4	71.6			1	71.8	61.0
		2.	24.9	2.0			2.	29.4	30.0			-2 -	22.9	35.8			2	93.1	75.3
		ŝ	68 9	73 3				22.4	301			-2 -	27.5	49.5			,	159.0	119.6
		6 +	14.4	17.8			5 *	22.8	45.6			-1	73 4	55 6			1	195 5	116 9
		ž	72.0	82.1			6 *	10.6	26.8			ĭ	177 1	150 4			6	124.4	119.2
0	6	ó	477.4	443.3			7	7.9	18.4			2	37.2	38.4			7	60.5	78.4
	-	1 *	20.6	15.1	1	4.	-7	17.2	37.2			3	156.1	143.6	2		5 - Ż	42.9	65.5
		2	328.9	347.9		÷.,	-6	42.9	70.3			ś	83.7	78.1	-		-6	69.3	78.9
		3*	27.8	18.9			-5 *	25.1	46.3	1	12	-5	29.7	41.8			-5	99.3	92.9
		4	192.6	191.7			-4	85.3	75.6			-4	19.1	28.3			-4	142.4	122.1
		5 *	24.7	15.3			-3 *	20.8	5.2			~3*	19.3	1.1			-3	147.2	119.3
		6	101.0	97.9			-2	107.3	88.4			~2 *	24.8	7.3			-2	118.0	79.7
		7	21.5	42.2			-1	53.1	45.3			-1 *	18.0	26.8			-1	146.6	110.6
0	7	1	137.7	136.0			0	136.3	144.2			0 *	25.9	20.8			0	* 36.0	20.1
		2	115.2	115.2			1.*	16.3	28.2			1.	22.2	5.3			1	* 21.5	14.9
		2	180.6	179.3			2	143.0	125.8			2 -	23.5	21.0			2	* 25.7	30.0
		-		95.8			2	07.3	73.4			3.	15.5	18.1			2	69.7	76.0
		2	121.4	134.1			2	99.3	63.9	1	12	~? *	02.1	76 7			4	107.2	02.2
0	8	ň	31 5	04.1			6	66 0	99.9			-2 -	21.0	11.0			5	13.7	22.2
	•	ĭ	70.9	69.6			7	24.2	32.3			0 *	93 6	4.2			2	94.8	32 1
		2	29.5	43.4	1	5.	-7	53.1	58.1			1 *	22.6	6.2	2		6 -6	70.0	76.4
		3	77.8	84.5		Ĩ.,	-6	41.8	67.1			2 *	20.3	19.6	-		-5	103.9	97.5
		4	58.3	70.5			-5 *	25.7	30.8			3 *	17.4	26.3			-4	73.0	57.4
		5	27.3	37.6			-4	141.4	118.6	1	14	-3	81.6	98.0			-3	221.1	203.4
		6	28.8	42.4			-3 *	24.7	23.6			-2	35.5	29.7			-2	* 48.4	54.1
0	9	1	309.1	306.3			-2	138.4	127.8			-1	81.1	85.9			-1	310.1	309.2
		2 *	20.0	13.1			-1	149.2	156.9			0	68.4	68.7			0	95.4	100.6
		2	175.4	182.8			0	50.2	59.0			1	24.5	25.0			1	297.4	331.8
		2	20.9	14.0			1	1//.4	204.2			2 *	10.6	24./			2	123.7	129.0
		6	25 0	25.5			ŝ	175.4	193.9		15	-2 +	13.0	26.4			2	06.5	Q1 0
0	10	õ	129.9	123.3			í.	45.9	30.4	•	.,	2 *	15.7	5.3				170.0	163.1
	-	1 *	22.8	35.5			5	133.8	103.8	2	0	-7 *	27.9	15.6			6	26.4	36.3
		2	109.7	106.9			6 *	11.9	22.3			-6	109.2	88,8	2		7 -6	89.8	107.2
		3	46.3	54.7			7	64.8	84.4			-5	126.2	96.4			-5	123.8	114.6
		4	95.5	95.3	1	6.	-7	17.6	37.2			-4	38.5	16.3			-4	119.4	102.4
		5	24.5	30.0			-6	31.3	40.6			-3	294.5	287.2			-3	176.4	152.8
			91.4	97.7			-5	63.4	78.1			-2	75.2	40.4			-2	86.2	81.6
Q,	11	1 -	35.7	27.8		-	-	25.0	40.0			-1	339.6	358.4			-1	139.0	117.1
		2*	20.5	14.5		•	* د	30.7	12.2			1	401.0	283.7 103 0			0	99.8	101.4
		2	30.0	1.9			-2	63 6)4.1 63 #			2	220.7	193.0			1	100.0	11.8
		5	26 9	31.7		-	- <u>1</u>	34.0	52.1			2	160.0	145.1			Ę	51 7	13 4
٥	12	ó	126.9	1 37.2			ĩ	28.5	36.8			5	164.4	169.7			- í.	120.5	98.8
•		1 *	18.0	5.6			2 *	20.0	9.9			6	41.9	59.4			5	* 26.4	26.1
		2	170.7	168.0			3 *	23.0	25.1			7	34.9	55.0			6	103.5	113.2
		3 *	17.1	15.3			Ĩ4	36.9	38.7	2	1	-7	61.1	61.5	2	1	B -6	42.5	23.2
		4	146.5	137.7			5 *	17.4	13.8			-6	142.5	132.0	-		-5	* 33.0	54.2
0	13	1	131.7	136.0			6 *	14.3	13.4			-5	149.2	164.3			-4	68.7	82.2
		2	28.5	12.1	1	7.	-6	27.3	53.0			-4	161.6	155.1			-3	55.2	8.4
		3	135.4	137.6			-5	42.2	76.4			-3	204.1	174.2			-2	88.7	55.6
		4	63.1	70.1			-4 *	23.3	26.6			-2	91.7	05.7			-1	50.3	27.8
U	14		10.4	2.0		-	<u>ر</u> -	107.2	113.0			-1	127.5	104.7				- 44.3	45.0
		· •	13 4	47.1				22.1	20.)			1	85.0	79.6				* 31 1	32 7
		3.	15.7	23.5			6	18.8	47.9			ŝ	61.5	42.3			ŝ	54 5	7.0
0	15	í	152.1	167.2			1 *	26.6	24.1			í.	119.5	113.2			í.	* 29.5	28.0
-		2	12.6	23.6			2 *	16.8	15.9			5	99.0	92.1			5	35.7	40.3
0	16	0	95.3	104.4			3	38.6	43.4			6	109.5	103.5			6	* 13.1	16.4
		1	11.5	32.8			4 *	19.7	15.0			7*	9.9	19.0	2		9 -6	35.2	45.7
1	1 .	-7	68.5	69.9			5	41.8	52.3	2	2	-7	82.4	82.6			-5	* 20.5	64.3
		-6	52.7	71.2			6	37.1	47.2			-6 *	44.7	42.2			-4	118.5	127.7
		-5	43.8	04.0	1	8.	-6 *	11.2	13.6			-5	68.2	75.8			-3	53.7	43.7

ь 2

Table 7. (Continued)

h	k	1	Sh. Pobe	Feal	1	h	k	1	Sh.P	Feel	۰ h	k	1	S. · F	P 1	ь	k 1	Ls	. · F	71
2	9	-2	180.2	208.3		3	3	2 *	15.0	6.9	з	11	3	54.2	55.8	4	5 9	,	12 0 08	50.8
		-1	64.9	72.0			1	3	24.3	3.5	,	**	4	96.9	95.0		1		10.7	4.3
		0	221.9	225.4				á.	21.9	13.1			5	34.2	45.0		í	(*)	12.0	6.3
		1	81.0	82.2				5	23.1	25.2	3	12	-4	12.7	18.3		5	5	39.8	44.6
		2	230.6	234.5				6*	7.6	4.3			-3	45.0	55.7		ē	ś.*	8.8	2.1
		3	87.0	72.7		3	4 -	?	53.2	56.3			-2	19.0	27.1	4	6 -6	5	21.4	26.1
		4	183.6	170.0			-	6	27.2	27.7			-1	21.1	24.7		-5	5 1	119.7	118.4
		2	41.2	46.2			-	5	87.1	82.9			0	29.1	32.6		-4	4	80.5	71.6
		0	67.9	73.8			-	4	41.3	9+5			1	* 10.4	3.7		-3	3	134.5	115.5
2	10	-?	118.3	129.0			-	3	115.6	104.2			2	27.4	22.5		-2	2	183.4	170.0
		3	138 5	150 6			-	2 -	14.7	10.1			2	* 7.5	8.7		-1		141.4	120.5
		_2	87 3	105.8			-		10 8	27.9	,	1)	-2	10.9	10.7				240.0	242.0
		-1	121.6	128 1					10.7	31 0			-î.	24.9	70 7				041.7	13/-9
		ō	* 53.5	72.7				2	56.1	58.5			ō	25.1	97.0		-		1 70 7	135 9
		1	131.6	121.7				3	79.0	71.5			ĩ	18.4	35.8		í	í i	1 30.4	120.3
		2	45.5	11.0				4	31.1	27.9			2	15.4	4.8			5	92.3	92.7
		3	134.2	133.6				5	80.3	82.9			3	* 5.2	4.2		é	ś	65.9	69.5
		4	44.2	40.4				6	16.1	7.9	3	14	-3	49.8	59.1	4	7 -6	6	91.5	100.7
		5	116.8	100.4		3	5 -	6	29.8	29.8			-2	15.0	11.9		-5	5	83.7	86.1
2	11	-5	* 18.2	6.4			-	5	30.0	33.6			-1	63.8	70.2		-4	i ا	149.6	134.5
		-4	42.8	28.2			-	4	127.9	106.2			0	14.7	20.0		-3	3	135.4	122.7
		-2	42.8	54.2			-	3	37.8	40.2			1	98.8	101.8		-2	2 :	198.7	184.4
		-2	* 30.2	51.0			-	2	132.0	128.3	-		2	* 8.9	4.1		-1		88.9	81.7
		-1	* 36 7	70.2			-	1	407.9	.05.5	,	12	-1	11.4	19.2				143.8	145.0
		ĩ	* 33.6	31.5				ĭ *	11.9	7.0			1	27.5	36.6		1	L 3	43.0	42.0
		2	* 10.7	11.5				2	163.9	169.3	4	0	-7	75.3	100.0		-	τ.	75 5	74.8
		3	53.6	40.2				3	66.0	61.6			-6	51.9	51.8		í	. *	11.3	9.7
		Å.	* 19.6	12.3				4	167.4	156.8			-5	121.7	133.9			5	72.1	70.7
		5	15.3	2.4				5	49.4	48.4			-4	83.3	83.9	4	8 -5	5	28.9	36.9
2	12	-4	68.3	80.7				6	73.8	77.1			-3	162.0	156.8		-4	4	53.9	59.5
		-3	93.3	101.7		3	6 -	6	31.0	30.6			-2	218.8	217.7		-3	3	73.8	67.4
		-2	56.5	56.9			-	5	48.2	52.8			-1	112.5	102.6		-2	2	59.7	59.1
		-1	190.4	204.2			-	4	60.7	57.4			1	129.4	148.1		-1	L :	101.0	89.6
			- 40.8	29.1			-) 	57.0	54.0			2	240.7	262.3		C .	. *	28.2	19.2
		5	230.3	215.4			-	2 -	20.0				2	157.0	180,4		1		19.2	4.4
		3	192 7	115 0			-	<u>.</u>	95.0	34 0				105.0	100 6			2	22.0	20.)
		í.	* 17.5	21.5				ĭ *	10.8	8.6			6	B1.1	87 4		ŝ	2	21.3	25 5
2	13	-4	53.9	64.3				2	51.8	49.6	4	1	-6	73.9	78.4			÷ •	7.8	4.1
		-3	76.7	97.5				3	23.2	3.2		-	-5	* 32.3	48.7	4	9 - 9	ś	37.3	41.8
		-2	91.3	103.2				i.	40.5	37.9			-4	161.0	160.3		-4	í.	108.1	119.1
		-1	117.6	108,2				5	50.4	44.1			-3	76.9	73.8		-3	5	72.1	75.8
		0	100.7	104.9				6	25.2	35.8			-2	260.7	252.1		-2	2 :	100.8	103.9
		1	* 28.0	32.2		3	7 -	6	85.4	97.3			-1	44.4	51.0		-1	L 3	169.2	162.1
		2	86.9	87.9			-	5	21.8	3.7			0	141.0	155.8		C) :	100.5	91.2
		2	- 10.2	10.3			-	4	83.5	67.4			1	* 6.0	11.3		1		185.1	191.0
•			75.7	47.9			-	2	22.4	43.2			2	* 11.0	9.9		2		113.5	110.9
-	14	-2	27.6	10.4			-	ĩ	77.5	60.0			2	* 12.0	19 /		ŝ	2.	02.9	123.0
		-1 -	• 23.8	23.6			-	ñ	128.6	121.6			-	83.0	79.0		5		72.5	85 0
		ō	+ 30.9	11.5				ī *	11.5	32.4			6	19.4	22.3	4 1	10 -5	ś	84.5	99.2
		1	24.5	21.5				2	51.5	58.2	4	2	6	90.8	93.9		-4	í.	26.0	46.0
		2	* 26,2	15.5				3	27.3	29.8			-5	136.9	126.0		-3	3 1	142.8	162.4
		3	89.8	7.5				4	35.8	38.6			-4	136.5	118.5		-2	2	54.0	67.9
2	15	-2	59.5	79.1				5*	7.0	18.1			-3	145.0	142.7		-1	L :	157.6	161.8
		-1	40.3	44.2			~	6	63.8	70.0			-2	36.4	40.8		0)	79.4	73.7
			50.3	66.2		3	8 -	5	23.8	26.2			-1	154.4	136.8		1	. :	112.3	107.0
		1	07.6	101 9			-	2	22.1	21.2				24.3	23.3		2	2.	51.9	58.0
۰.	•	- <u>-</u> 7	* 67	3 4			-	2	53 3	50 6			-	* 10.0	79.9		2	2	67.0	65.1
1	-	-6	71.5	69.0			_	ź *	15.3	26.0			3	• 10.9	13.1		5	5	32.3	38.5
		-5	30.3	24.4			-	1	147.6	141.6			á	50.5	55.5	4 1	11 -4	í	31.2	41.1
		-4	124.6	127.0				0	26.0	12.7			5	43.2	37.9		-3	5 *	13.1	6.9
		-3	23.9	24.2				1	184.6	187.6			6	37.1	42.0		-2	2	24.4	25.7
		-2	143.1	149.4				2*	11.1	3.2	4	3	-6	127.7	136.4		-1	ι*.	26.1	25.7
		-1	52.4	50.1				3	133.0	130.8			-5	29.1	24.8		C)	33.5	39.3
		0	130.1	145.5				4	28.9	34.8			-4	104.5	95.9		1	.*	7.8	5.0
			- 10,4 160 P	10.1				6	36 1	60.7			-)	104.9	141.2		2	4 K	39.7	40.4
		÷.	* 12.8	5.4		٦.	۹.	š	47.0	58.0				216 6	211 1		2	<i>.</i>	15 5	11 0
		á	124.3	125.3			12	4	27.8	31.4			ō	205.0	216.9	4 1	12 -4		29.4	46.2
		5	* 13.5	19.6				3	30.5	25.9			ī	236.1	245.1	• •	-1	5	53.4	64.3
		6	75.6	76.4				2 *	9.9	10.2			2	210.9	204.7		-2	2	72.6	78.7
		7	* 6.2	7.5			-	1	76.2	75.1			3	242.5	238.8		~1	ι :	107.6	104.8
3	2	-7	84.1	82.8				0	44.7	30.3			4	151.2	152.5		0)	79.3	78.8
		-6	25.9	36.6				1 *	7.0	7.0			5	118.8	128.8		1	. :	105.8	106.6
		-5	72.3	65.7				2	22.5	16.6			6	84.5	89.6		2	2 :	127.7	122.1
		-9	99.1	39.7				* ز	10.0	1.8	4	4	6	88.4	96.1		. 3	2	74.4	73.1
		2	70.b	40.7				4 E	20.3	15.0			-5	157.0	155.4	9 1	ני <ו גי	2	77.3	89.0
		-1	166 3	156.6		31	0	ś	58 0	79 4			3	210 0	77.7		-2	ĩ	66.8	66 5
		õ	33.2	15.1		· ·	1	í *	15.6	14.5			-2	39.2	23.5			5	93.3	93.6
		1	147.8	166.3			-	ŝ	95.0	105.2			-1	175.3	157.6		ĩ	i	85.1	79.1
		2	55.5	50.7			-	2	45.6	48.4			0	41.2	37.2		2	2	79.5	75.5
		3	98.0	91.9			-	1 *	18.8	20.1			1	126.7	139.5		3	5	73.4	69.6
		4	34.9	24.8				0 *	13.7	27.0			2	48.9	60.3	4 1	14 0	•	10.4	3.2
		5	105.9	106.7				1 *	7.1	8.0			3	54.9	56.3	-	-1	Ļ	16.8	25.0
		5	40.6	44.8				2*	11.1	14.0			4	62.2	59.3	5	1 -6	*	10.9	10.7
	-	7	/2.5	90.4				ز	53.3	51.8			5	26.6	20.7		-5	2	55.0	68.9
ر	,	-6	- 0.0	10.8				2	42.0	42.0 95 è		5	_6	1.3	70.9		-4	1	39.1	42.4
		-5	19.2	14.9		, ,	• •	2	22.2	27.0		2	-5	37.8	18 0			<u>;</u>	32 6	33.0
		-	* 16.5	17.1			-	5	65.1	67.7			4	142.8	133.4		_1	ĭ	54.9	80.8
		- <u>5</u> -	· 21.0	19.5				ź	48.1	52.9			-3	* 28.2	4.2			5	76.1	83.2
		-2	* 13.9	11.5			-	1	71.1	68.7			-2	164.4	153.4		1	L 3	206.1	86.8
		-1	71.7	62.7				0	92.2	85.4			-1	* 17.7	10.3		2	2 :	106.5	115.2
		Ó	39.7	33.3				1	23.1	21.3			0	103.2	95.2		3	5	51.5	65.0
		1	- 10.7	15.0				2	92.4	88.8			1	* 0.8	3.5		4	•	12.7	05.9

Table 7. (Continued)

h	k J	L 8.	· .	F.	b	k	1		S. • F .	P.		h	k 1	S. · P		F .	ь	k	1	S. F.	Ρ.
-		. '	n 688	Cal	-				0 008	Cal		-		- <u>h</u> -o	ba	cal		-		A obs	641
2	1	Ş	/1.0	77.9	2	> 0			20.1	14.5	5	5	13 0	38.0	5	45.0	6	5	-2	51.4	27.3
			32.7	48.0				2.	10.4	1.4		~	. 1	8.	2	5.8			-1	122.3	104.6
5	2 -0	<u>b</u>	30.7	44.3			4		8.6	3.4	2	0	0 -6	128.	7	100.4			0	47.0	37.6
		2	19.4	12.1	_		2		44.0	42.2	-		-5	41.	Ç.	45.1			1	43.3	58.1
	-4	1	12.4	113.2	5	7	-5	5	61.8	60.9	,		-4	118.0	5	111.1			2	20.4	28.4
	-3		19.4	28.5			-4		23.8	33.0)		-3	* 18.9	9	35.7			3	* 13.0	4.5
	-2	2 1	06.0	128.3			-3	i –	93.7	97.1			-2	145.9	Э	150.0			4	* 8.4	12.9
	-1	ι :	50.3	63.4			-2	: :	70.0	65.0)		-1	82.1	L	88.3			5	* 6.4	3.0
)	77.9	83.9			-1	•	17.7	22.5	5		1	103.2	5	115.5	-6	6	-5	20.6	23.3
	1	1	46.2	45.9			0)	85.1	80.6	3		2	186.0	6	192.1			-4	124.8	124.6
		21	18.5	127.5			1		31.0	8.9)		- 3	144.	3	142.5			-3	* 20.5	18.1
		5	64.7	67.2			- 2		72.2	68.6			4	141.4	4	140.4			-2	135.8	133.2
		۱	06.0	117.3			3		59.7	62.0	,		5	81.	9	78.1			~1	86.9	72.4
	5	5	70.3	71.0			- 4		41.8	46.4		6	1 -5	117.3	3	117.9			0	168.4	154.9
	é	5.	49.4	51.3			5		49.2	52.7	,		-4	76.8	3	68.8			1	123.4	108.2
5	3 -6	5	13.1	18.6	5	8	-5	*	6.9	16.5			-3	156.8	3	153.8			2	169.8	156.1
		5	33.8	42.6			-4		53.8	58.1			-2	* 17.8	3	21.8			3	109.7	97.
	_1		37.6	35.4			- 1	*	19.8	10.0))		-1	1 32.	3	141.2			4	127.7	121.0
		ŝ	32.7	24.7			-2		58.6	68.0			ō	32.	ŝ	26.0	6	7	-5	85.3	118.1
		÷ * •	14.1	10.6			_1	· *	16.6	9.9			1	102.5	ž.	121 6	-		-ú-	* 14.0	39
	-1		13.3	14.6			ĉ		67 6	71 0			â	35 6	5	14 1				197 8	178
			16 1	13.6					7	67.0			ĩ	39.0	,	EV 0			~	* 07 E	1,0.
			10.1	1 2					103 7	107.0			2	* 13 9	2	10 6				120.8	1 69 0
	- 2		76 1	11.0					101 7	103.1			2			10.4			-1	170.0	1,00
			10.0	22.0					101.3	105 0		6	a 2		3	4.4				166 6	
			11.0				4		74 1	104.0		0	2 - 2	* 19.0	2	14.5			1	104.0	151.1
			11.0	10.2	-		. 2		70.4	10.1			-4	- 17 1		141.2			2	- 14.2	29.5
	2	2 * :	10.0	11.2	2	, ,			29.4	42.4			- 2	* 17.4		14.2			2	88.0	89.
~		2.	10.0	13.9			-2	2	51.1	22.0	2		-2	109.	2	162.8		~		14.0	20.0
2	4 -0	2	(2.2	80.3			-2	1	12.0	10.0			-1	T 13.5	9	0.4	0	8	-4	05.0	79.3
			22.9	23.2			-1		11.9	24.			0	133.9	9	119.9			-2	• 10.3	2.3
	-9		90.4	88.0			- 0		29.0	32.3	5		1	19.0		24.8			-2	75.2	81.7
		2.	70.1	/4.0			1		15.3	3.0	,		2	39-	<u>(</u>	55.7			-1	* 22.3	22.3
	-2	2 1	13.8	100.8			- 2		39.8	45.1			3	* 13.1	L	10.7			0	84.3	59.1
	-1	1	05.7	92.0			- 3	*	10.3	4.0	,		4	23.8	5	34.2			1	* 18.5	7.5
		0 1	06.3	108.3	_		4	ŧ.	11.1	11.	5		5	35.9	9	34.5			2	53.5	54.3
	1		45.0	45.4	5	5 10	-4	ł.	26.0	41.8	2	6	3 -5	130.2	2	129.6			3	* 9.2	6.0
		2	73.0	73.4			-3	i –	56.1	61.6	>		-4	* 11.	5	2.0			4	8.0	10.1
		5	31.1	25.4			-2	2	31.6	40.2	2		3	138.4	<u> </u>	157.0	6	9	-4	* 11.3	7.6
	4	÷ •	46.0	52.6			-1		60.7	63.7	,		-2	73.0	6	61.9			-3	87.9	94.1
	5	5	27.1	33.8			0	•	60.4	66.9)		-1	118.0	9	120.0			-2	35.0	38.
		5 :	54.7	55.7			1		55.1	57.0)		0	178.2	5	146.2			-1	129.9	127.6
5	5 -6	j *	5.1	7.1			- 2		24.4	16.4			1	126.9	9	141.5			0	71.3	61.8
	-5	5	49.2	47.5			- 3	*	9.7	18.1			2	113.	5	116.0			1	143.5	127.
	-4	** * :	19.2	18.8			4	• *	5.3	7.3	5		- 3	154.	5	170.1			2	89.1	83.4
	-3	5	36.9	34.5	5	11	-3	i –	55.0	56.3	5		4	44.6	6	49.6			3	93.2	98.0
	-2	s * :	19.2	22.7			-2	*	11.4	21.6	i		5	107.9	9	112.3	6	10	-2	112.0	122.3
	-1	1	26.0	128.4			-1		97.7	88.9)	6	4 - 5	* 11.	7	15.5			-1	* 16.8	19.0
	0)	51.6	46.8			0		26.4	17.4	1		-4	130.8	3	128.9			0	135.6	127.7
	1	1	44.4	150.9			1		115.5	107.3	\$		-3	28.	3	51.2			1	* 12.7	15.3
	2	2 '	71.1	73.2			2	*	12.0	19.9	2		-2	186.2	2	190.4			2	71.6	82.1
	3	5.	71.4	79.2			3		91.6	94.4			-1	53.7	7	32.5			3	16.9	22.0
	4	<u>نا</u>	75.6	71.3	5	12	-3	5	32.5	34.1			0	166.	9	159.3	6	11	-2	34.9	37.3
		5	72.9	73.7			-2	*	10.9	12.3	5		1	34.9	9	34.3			-1	38.2	45.
5	6 -	5.	45.1	42.8			-1		57.7	58.8	3		2	49.0	6	53.7			ō	* 16.8	6.
÷.	-i	. * :	18.5	15.5			ē		15.2	5.9)		3	* 15.0	6	6.4			1	* 10.4	8.
		3	36.7	40.9			1		37.9	39.	,		ű.	27.8	8	39.0			2	32.3	34.0
	-2		13.7	6.8			2		13.4	12.1			5	33.	7	41.2	6	t 2	-1	47.0	46.
	-1		95.9	93.2			-		17.7	20.	5	6	5 - 5	36.	2	60.6			ō	42.9	52.0
	ĉ	j,	42.4	27.5	5	13	-2		57.1	60.0		-	-4	55.	2	51.4			ī	70.5	20.1
	1		13.8	7.9			_1		21.7	26	,		_3	60.1	i	71.4			-	,	,
	- · ·										-		,		-						
*	Unobs	erva	ble in	tensity:	one hal	f 🗉	ini	mur	a deteci	able w	alue.										

Results of the refinement

The asymmetric unit of marrite contains three metal atoms and three sulfur atoms, all located in the general position. The values obtained for the atomic positions are given in Table 5. The displacements from the ideal substructure are also indicated. These are particularly marked for the S atoms and amount to as much as 1.09 Å. Values for the anisotropic temperature-factor coefficients which were obtained are presented in Table 6, with values for the equivalent isotropic temperature factor

$$B = \frac{4}{3} \sum_{i} \sum_{j} \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j).$$

The latter values closely correspond to those obtained from refinement with isotropic temperature factors (Table 5).

The observed structure factors and those calculated with the parameters of Tables 5 and 6 are compared in Table 7.

Discussion of the structure

A composite map of electron-density sections through the centers of atoms in the asymmetric unit of marrite is given in Fig.4. A subnet passing through the ideal substructure positions has been included in this map, and serves to indicate the marked displacement of the atoms from these positions. The atomic arrangement differs from that reported for freieslebenite (HELLNER, 1957) in both the placement of the inversion center in the structure, and the distribution of metal atoms. The crystal structure of freieslebenite is currently being refined (CHO and WUENSCH, to be published).



Fig. 4. Composite of electron-density sections through the atoms in the asymmetric unit of marrite. Contour interval 7.9 $e/Å^3$ for sulfur atoms, 15.7 $e/Å^3$ for metal atoms; zero contour dotted. The subnet has been drawn through the ideal substructure locations for the atoms

The structure of marrite superficially resembles the PbS arrangement. All atoms, to a first approximation, are in octahedral coordination. The details of the coordination polyhedra are presented in Fig. 5. Bond lengths and angles, with estimated standard deviations, are summarized in Tables 8 and 9.

The distortions of the ideal arrangement are such that As has only three nearest S neighbors at distances of 2.26, 2.27 and 2.28 Å. The three additional neighbors are at significantly larger distances of from 3.29 to 3.79 Å. These distances are comparable to the sum of the van der Waals radii, 3.85 Å, given by PAULING (1960). The three bonds are nearly orthogonal and range from 97.3° to 99.3°. Such coordination is invariably found for As in sulfosalts, and is characteristic of covalent bonding involving the p^3 valence electrons of As. The short and long bond lengths are similar to those observed in



Fig. 5. Coordination polyhedra in marrite. (a) Arrangement of sulfur atoms about the metal atoms. (b) Arrangement of metal atoms about the sulfur atoms

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		(11041050-1101g				
		As		Pb		Ag
	S(2)''	$2.259 \pm .014$ Å	S(3)'''	$\textbf{2.799} \pm .013 \text{ \AA}$	S(2)'	$2.473 \pm .014$ Å
	S(3)	$\textbf{2.269} \pm .015$	S(1)'	$\textbf{2.837} \pm .014$	S(2)	$\textbf{2.518} \pm .015$
Metal-atom	S(1)	$\textbf{2.279} \pm .015$	S(1)	$\textbf{2.962} \pm .013$	S(1)'''	$\textbf{2.682} \pm .014$
polyhedra	S(1)'	$3.292\pm.015$	S(3)'	$\textbf{2.976} \pm .014$	S(3)	$\textbf{2.912} \pm .015$
	S(2)'	3.645 ± 0.15	S(2)	$\textbf{3.136} \pm .014$	S(3)'	$\textbf{3.395} \pm .015$
	$\mathrm{S}(2)^{\prime\prime\prime}$	$3.787\pm.013$	S(3)''	$\textbf{3.260} \pm .013$	S(1)''	$3.451 \pm .014$
		S(1)		S(2)		S(3)
	As	$2.279 \pm .015$ Å	As''	$2.259 \pm .014$ Å	As	$2.269\pm.015$ Å
	Ag'''	$\textbf{2.682} \pm .014$	Ag'	$\textbf{2.473} \pm .014$	Pb'''	$\textbf{2.799} \pm .013$
Sulfur-atom	Pb'	$\textbf{2.837} \pm .014$	Ag	$\textbf{2.518} \pm .015$	Ag	$\textbf{2.912} \pm .015$
polyhedra	Pb	$\textbf{2.962} \pm .013$	Pb	$\textbf{3.136} \pm .014$	Pb'	$\textbf{2.976} \pm .014$
	As'	$3.292\pm.015$	$\mathbf{As'}$	$3.645\pm.015$	Pb''	$\textbf{3.260} \pm .013$
	Ag''	$3.451\pm.014$	As'''	$3.787 \pm .013$	Ag'	$\textbf{3.395} \pm .015$

 Table 8. Interatomic distances in marrite

 (Nearest-neighbor bonds are in bold face)

	As	Pb	Ag
Metal-atom polyhedra	$\begin{array}{lll} S(1) & -As{-}S(2)^{\prime\prime\prime} & 68.4^{\circ}\pm.4^{\circ}\\ S(1)^{\prime} & -As{-}S(2)^{\prime\prime} & 75.9^{\circ}\pm.3^{\circ}\\ S(2)^{\prime} & -As{-}S(3) & 77.5^{\circ}\pm.4^{\circ}\\ S(2)^{\prime} & -As{-}S(2)^{\prime\prime} & 80.6^{\circ}\pm.6^{\circ}\\ S(1) & -As{-}S(1)^{\prime} & 82.3^{\circ}\pm.6^{\circ}\\ S(2)^{\prime\prime\prime}{-}As{-}S(3) & 92.3^{\circ}\pm.4^{\circ}\\ S(1)^{\prime} & -As{-}S(2)^{\prime\prime} & 93.0^{\circ}\pm.5^{\circ}\\ S(1)^{\prime} & -As{-}S(3) & 97.3^{\circ}\pm.6^{\circ}\\ S(1) & -As{-}S(2)^{\prime\prime} & 97.9^{\circ}\pm.5^{\circ}\\ S(1) & -As{-}S(3) & 99.3^{\circ}\pm.5^{\circ}\\ S(2)^{\prime\prime\prime} & -As{-}S(3) & 99.3^{\circ}\pm.5^{\circ}\\ S(1)^{\prime} & -As{-}S(2)^{\prime\prime} & 103.2^{\circ}\pm.3^{\circ}\\ S(2)^{\prime\prime} & -As{-}S(2)^{\prime\prime\prime} & 113.9^{\circ}\pm.4^{\circ}\\ \end{array}$	$\begin{array}{lll} & S(2) & -Pb - S(3)'' & 65.3 \ ^{\circ} \pm .3 \ ^{\circ} \\ & S(1)' - Pb - S(3)' & 71.9 \ ^{\circ} \pm .4 \ ^{\circ} \\ & S(1) & -Pb - S(1)' & 80.4 \ ^{\circ} \pm .5 \ ^{\circ} \\ & S(1)' - Pb - S(3)''' & 81.3 \ ^{\circ} \pm .4 \ ^{\circ} \\ & S(2) & -Pb - S(3)'' & 81.4 \ ^{\circ} \pm .3 \ ^{\circ} \\ & S(3)' - Pb - S(3)''' & 81.8 \ ^{\circ} \pm .5 \ ^{\circ} \\ & S(1) & -Pb - S(3)''' & 82.4 \ ^{\circ} \pm .4 \ ^{\circ} \\ & S(3)' - Pb - S(3)''' & 88.5 \ ^{\circ} \pm .5 \ ^{\circ} \\ & S(2) & -Pb - S(3)''' & 98.3 \ ^{\circ} \pm .4 \ ^{\circ} \\ & S(1)' - Pb - S(3)''' & 110.0 \ ^{\circ} \pm .4 \ ^{\circ} \\ & S(1) - Pb - S(3)''' & 112.6 \ ^{\circ} \pm .4 \ ^{\circ} \\ & S(1) - Pb - S(2) & 126.4 \ ^{\circ} \pm .4 \ ^{\circ} \end{array}$	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$
	S(1)	S(2)	S(3)
Sulfur-atom polyhedra	$\begin{array}{cccccc} Pb & -S(1)-Ag'' & 67.5^{\circ}\pm.3^{\circ} \\ As' & -S(1)-Pb & 68.2^{\circ}\pm.3^{\circ} \\ Ag''-S(1)-As' & 69.5^{\circ}\pm.3^{\circ} \\ Pb' & -S(1)-Ag'' & 78.0^{\circ}\pm.3^{\circ} \\ As' & -S(1)-Pb' & 82.4^{\circ}\pm.4^{\circ} \\ Ag''-S(1)-As & 83.8^{\circ}\pm.4^{\circ} \\ Ag'''-S(1)-As' & 86.4^{\circ}\pm.4^{\circ} \\ Ag'''-S(1)-Pb' & 94.0^{\circ}\pm.5^{\circ} \\ Pb & -S(1)-Pb' & 94.0^{\circ}\pm.5^{\circ} \\ Pb & -S(1)-Pb & 100.5^{\circ}\pm.5^{\circ} \\ Pb' & -S(1)-Ag''' & 107.7^{\circ}\pm.5^{\circ} \\ Ag'''-S(1)-As & 119.7^{\circ}\pm.6^{\circ} \\ Pb & -S(1)-Pb & 140.5^{\circ}\pm.5^{\circ} \\ \end{array}$	$\begin{array}{rll} As' & -S(2) - Pb & 61.9 \ ^\circ \pm .2 \ ^\circ \\ As' & -S(2) - As''' & 66.1 \ ^\circ \pm .3 \ ^\circ \\ As''' - S(2) - Pb & 67.8 \ ^\circ \pm .3 \ ^\circ \\ Ag' & -S(2) - As''' & 79.1 \ ^\circ \pm .4 \ ^\circ \\ Ag & -S(2) - As''' & 83.3 \ ^\circ \pm .4 \ ^\circ \\ Ag' & -S(2) - As' & 83.9 \ ^\circ \pm .4 \ ^\circ \\ Ag' & -S(2) - Ag' & 94.0 \ ^\circ \pm .5 \ ^\circ \\ As'' & -S(2) - Pb & 98.5 \ ^\circ \pm .5 \ ^\circ \\ As' & -S(2) - As'' & 99.4 \ ^\circ \pm .5 \ ^\circ \\ Pb & -S(2) - Ag' & 108.7 \ ^\circ \pm .6 \ ^\circ \\ Ag & -S(2) - Ag' & 110.3 \ ^\circ \pm .6 \ ^\circ \\ Pb & -S(2) - Ag' & 139.4 \ ^\circ \pm .5 \ ^\circ \\ \end{array}$	$\begin{array}{ccccc} Ag' & -S(3) - Ag & 70.3 \ ^\circ \pm .3 \ ^\circ \\ Pb'' & -S(3) - Ag & 70.8 \ ^\circ \pm .3 \ ^\circ \\ Pb'' & -S(3) - Ag' & 73.5 \ ^\circ \pm .3 \ ^\circ \\ Pb' & -S(3) - Ag' & 89.2 \ ^\circ \pm .4 \ ^\circ \\ As & -S(3) - Pb' & 90.6 \ ^\circ \pm .5 \ ^\circ \\ Pb' & -S(3) - Pb'' & 91.5 \ ^\circ \pm .4 \ ^\circ \\ Pb''' & -S(3) - Ag' & 91.5 \ ^\circ \pm .4 \ ^\circ \\ As & -S(3) - Pb'' & 94.9 \ ^\circ \pm .5 \ ^\circ \\ Pb''' & -S(3) - Ag & 95.2 \ ^\circ \pm .4 \ ^\circ \\ Pb' & -S(3) - Pb''' & 98.2 \ ^\circ \pm .4 \ ^\circ \\ Pb' & -S(3) - Pb''' & 98.2 \ ^\circ \pm .4 \ ^\circ \\ As & -S(3) - Pb''' & 100.0 \ ^\circ \pm .5 \ ^\circ \\ Ag & -S(3) - As & 106.9 \ ^\circ \pm .5 \ ^\circ \end{array}$

Table 9. Bond angles in marrite

Angles between pairs of bonded atoms are indicated in **bold** face.

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Structure	Atom	Coordination number	Range of bond lengths for six nearest neighbors	Additional neighbor(s)	References
Marrite PbAgAsS ₃	Pb	6	2.80 to 3.26 Å	> 4.11 Å	Present work
$\rm Hutchinsonite~(Tl,Pb)_2As_5S_9$	Pb,Tl(1)	7	2.77 to 3.28	3.43	Таке́исні et al. (1965)
Rathite I					
$\rm (Pb,Tl)_3As_4(As,Ag)S_{10}$	Pb,Tl(3)	7	$2.80 ext{ to } 3.14$	3.39	MARUMO and NOWACKI (1965)
$Gale no bismutite \ \mathbf{PbBi}_2\mathbf{S_4}$	Pb	8	$2.85 ext{ to } 3.21$	3.21, 3.76	IITAKA and NOWACKI (1962)
Meneghinite substructure	Pb	7	2.89 to 3.12	3.30	Euler and Hellner (1960)
$\mathrm{CuPb_{13}Sb_7S_{24}}$	Pb	7	2.83 to 3.31	3.31	
Aikinite	Pb,Bi(A)	7	$2.84 ext{ to } 3.12$	3.35	Wickman (1953)
CuPbBiS ₃	Pb,Bi(B)	7	2.88 to 3.16	3.16	
Jamesonite	Pb(1)	8	2.91 to 3.13	3.29, 3.39	NIIZEKI and BUERGER (1957)
$\mathrm{FePb_4Sb_6S_{14}}$	Pb(2)	7	$2.85 ext{ to } 3.08$	3.28	
Dufrenoysite	Pb(5)	7	2.83 to 3.03	3.68	MARUMO and NOWACKI (1967 <i>a</i>)
$\mathrm{Pb_{16}As_{16}S_{40}}$	Pb(6)	7	2.82 to 3.07	3.73	
	Pb(7)	7	$2.87 ext{ to } 3.40$	3.75	
	Pb(8)	7	$2.84 ext{ to } 3.26$	3.60	
Hatchite					
$PbTlAgAs_2S_5$	Pb, Tl (1)	8	2.81 to 3.24	3.26, 3.31	MARUMO and NOWACKI (1967 b)

Table 10. Ranges of Pb-S bond lengths similar to those found in marrite

other structures which are superstructures based upon the PbS arrangement. (For example, smithite, $AgAsS_2$, Hellner and Burz-LAFF, 1964.)

The Pb coordination group is a distorted octahedron. The bond lengths range almost continuously between 2.80 Å and 3.26 Å. It is difficult to decide upon a division between nearest-neighbor and second-nearest-neighbor bonds. All eight neighbors of the second coordination sphere of the ideal PbS arrangement are at significantly longer distances (4.11, 4.19, 4.30, 4.42, 5.35, 5.35, 5.38, and 5.40 Å). Despite the irregularity of the Pb coordination polyhedron, a remarkably similar range of bond lengths have been observed in several other Pb sulfosalts, Table 10.

Nearest neighbors and second-nearest neighbors are also distinguishable in the coordination of the Ag atom. Three S are at distances of 2.47, 2.52 and 2.68 Å. These distances are close to 2.56 Å, the sum of the tetrahedral covalent radii (PAULING, 1960). This group of atoms and the Ag atom are nearly coplanar: the sum of the three bond angles is 357.2°. Two additional S are at distances of 3.40 and 3.45 Å. One additional S is an intermediate distance of 2.91 Å, and it is again difficult to decide whether or not this atom is completely bonded to Ag. This bond is approximately normal to the triangular group formed by Ag and the three nearest S neighbors. Together, these atoms results in a distorted tetrahedral coordination about the Ag atom. Despite the irregularities of this group, there is again a remarkable similarity between these bond lengths and those found in other Ag sulfosalts which are superstructures based on the PbS arrangement : 2.51, 2.56, 2.68 and 2.84 Å; 2.52, 2.55, 2.65 and 2.90 Å for Ag(1) and Ag(2) in smithite, AgAsS₂ (Hellner and Burzlaff, 1964), and 2.44, 2.50, 2.58, and 2.73 Å for Ag(1) in miargyrite, AgSbS, (KNOWLES, 1964). Similar distances have also been observed in sulfosalts with structures not based upon the PbS arrangement: 2.48, 2.52, 2.54 and 2.93 Å in hatchite, PbTlAgAs₂S₅ (MARUMO and NOWACKI, 1967b), and 2.48, 2.49, 2.76 and 2.96 Å for Ag(2) in xanthoconite Ag_3AsS_3 (ENGEL and NOWACKI, 1967).

The arrangement of metal atoms about the three sulfur atoms in the asymmetric unit is given in Fig.5*b*. An interesting feature of the structure is that the large displacements of the S atoms from their ideal substructure positions result in tetrahedral coordination for two of these atoms. The atom S(1) is coordinated by 1 As, 2 Pb and 1 Ag. The bond angles vary between 94.0° and 140.5°. The maximum devia-

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tion from the ideal tetrahedral angle of 109.47° is for the bond Pb-S(1)-Pb' which, in an undeformed structure, would be 180° . Atom S(2) is coordinated by 2 Ag, 1 Pb and 1 As. The bond angles range from 94.0 to 139.4° and correspond closely to those formed by





(b)

Fig. 6. Linkage in (001) of the coordination polyhedra formed by the arrangement of sulfur atoms about (a) metal atoms near $z = \frac{1}{4}$ and (b) metal atoms near $z = \frac{3}{4}$. The upper and lower edges of the Pb octadehra are translation equivalent and superpose in projection. The larger tetrahedron is the sulfur arrangement about Ag. The smallest polyhedron is the trigonal pyramid formed with As. The As location is indicated by a small circle.

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the bonds about S(1). The coordination of S(3) differs from that of the other two S atoms. Only five metal atoms (3 Pb, 1 Ag and 1 As) form bonds with S(3), and the angles between bonds are close to those for octahedral coordination. It is of interest to note that, of these five bonds, one is the abnormally long Ag-S bond, and one is the longest Pb-S bond. This atom should therefore be considered as entering into three normal bonds plus two bonds of partial strength.

Figure 6 indicates the manner in which the polyhedra formed by the S atoms about the metal atoms are linked in (001). Fig. 6*a* presents the polyhedra about metal atoms near $z = \frac{1}{4}$, and Fig. 6*b* the polyhedra about metal atoms near $z = \frac{3}{4}$. These two layers of polyhedra are connected through the sharing of certain edges.

Each PbS₆ octahedron in Fig. 6*a* shares one edge with an AsS₃ pyramid in the (001) plane. Another two edges are shared with a PbS₆ octahedron and an AsS₃ pyramid in a layer equivalent by translation to Fig. 6*b* at $z = -\frac{1}{4}$. Two additional edges are shared with the polyhedra in a layer near $z = \frac{3}{4}$ (Fig. 6*b*). One of these edges is shared with a second PbS₆ octahedron, and another edge with an AgS₄ tetrahedron. The PbS₆ octahedron thus shares a total of five of its eight edges: two with other PbS₆ octahedra, two with AsS₃ pyramids, and one with the AgS₄ tetrahedron. The AsS₃ pyramid shares two of the three edges in its base with PbS₆ octahedra, and the AgS₄ tetrahedron shares but one of its six edges with a PbS₆ octahedron.

Table 11 present the S—S distances in the metal atom polyhedra. These distances are, for the most part, comparable to, or greater than 3.70 Å, the van der Waals contact distance given by PAULING (1960). The S—S distances in the AsS₃ pyramid are exceptions. These separations are about 0.3 Å shorter than the sum of the van der Waals radii. This shortening occurs as a result of a balance between compression of the S atoms and distortion of the three As—S bonds from orthogonality. It has been observed (e.g., WUENSCH *et al.*, 1966) that, if As is replaced by Sb, the longer metal-sulfur bond permits bonds which are more nearly orthogonal and permits an increase in the S—S distance. Table 11 also indicates those edges which are shared with other polyhedra. Unlike ionic structures, in which shared edges tend to be shortened, there is little correlation between edge sharing and the lengths of the edges.

Crystallographically distinct metal-metal distances in the structure are presented in Table 12. All of these distances, particularly those between like metals, are greater than the sum of metallic radii (WELLS,

As ²	Pb			Ag ²			
Separation	Metal-atom polyhedron sharing edge	Sepa	ration	Metal-atom polyhedron sharing edge	A Separation		Metal-atom polyhedron sharing edge
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Pb Pb	$\begin{array}{c} S(1)'-S(3)'\\ S(2)-S(3)''\\ S(1)'-S(3)'''\\ S(1)-S(1)'\\ S(3)'-S(3)'''\\ S(1)-S(3)'''\\ S(2)-S(3)'\\ S(3)'-S(3)''\\ S(2)-S(3)''\\ S(1)'-S(3)''\\ S(1)-S(3)''\\ S(1)-S(2)\end{array}$	$\begin{array}{c} 3.416 \pm .018 \text{\AA} \\ 3.451 \pm .018 \\ 3.672 \pm .019 \\ 3.744 \pm .029 \\ 3.782 \pm .027 \\ 3.795 \pm .019 \\ 3.986 \pm .020 \\ 4.356 \pm .026 \\ 4.494 \pm .018 \\ 4.999 \pm .019 \\ 5.180 \pm .018 \\ 5.443 \pm .019 \end{array}$	As As Pb Ag Pb	$\begin{array}{c} S(1)^{\prime\prime} -S(2)\\ S(1)^{\prime\prime\prime} -S(2)\\ S(1)^{\prime\prime\prime} -S(3)\\ S(1)^{\prime\prime\prime} -S(3)\\ S(2)^{\prime} -S(3)\\ S(2)^{\prime} -S(3)\\ S(2)^{\prime} -S(3)^{\prime}\\ S(1)^{\prime\prime} -S(2)^{\prime}\\ S(2)^{\prime} -S(3)\\ S(1)^{\prime\prime\prime} -S(2)^{\prime}\\ S(2) -S(3)\\ S(1)^{\prime\prime\prime} -S(2)^{\prime}\\ S(2) -S(3)\\ S(1)^{\prime\prime\prime} -S(3)^{\prime}\\ S(1)^{\prime\prime\prime} -S(3) \end{array}$	$\begin{array}{c} 3.423 \pm .018\mathrm{\AA}\\ 3.630 \pm .018\\ 3.672 \pm .019\\ 3.795 \pm .019\\ 3.795 \pm .019\\ 3.856 \pm .020\\ 3.986 \pm .020\\ 4.090 \pm .019\\ 4.269 \pm .019\\ 4.269 \pm .019\\ 4.373 \pm .019\\ 4.849 \pm .027\\ 4.999 \pm .019\\ 5.180 \pm .018\\ \end{array}$	Pb

Table 11. Sulfur-sulfur contact distances in metal polyhedra

(Van der Waals contact distance = 3.70 Å)¹

¹ PAULING (1960).

² Contacts between pairs of sulfur atoms bonded to the metal atom are indicated in bold face.

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Contact Sum of metallic radii		Observe	Sulfur polyhedron where present	
Pb—Pb	3.50 Å	Pb'—Pb''' Pb'—Pb''	$4.367 \pm .005 ext{ \AA} \\ 4.470 \pm .005$	S(3) S(3)
Ag–Ag	2.88	Ag - Ag'	$\textbf{3.651} \pm .011$	S(2),S(3)
As—As	2.50	As'—As''' As'—As''	$\begin{array}{c} 4.053 \pm .012 \\ 4.590 \pm .009 \end{array}$	S(2) S(2)
Pb—Ag	3.19	Pb —Ag'' Pb'—Ag'' Pb'—Ag''' Pb'—Ag''' Pb —Ag	$\begin{array}{c} \textbf{3.586} \pm .006 \\ \textbf{3.985} \pm .006 \\ \textbf{4.217} \pm .006 \\ \textbf{4.457} \pm .006 \\ \textbf{4.482} \pm .007 \end{array}$	S(1), S(3) S(1), S(3) S(1), S(3) S(1), S(3) S(2), S(3)
Pb—As	3.00	Pb —As' Pb'—As Pb —As''' Pb —As Pb —As''	$\begin{array}{c} 3.516 \pm .007 \\ 3.762 \pm .007 \\ 3.897 \pm .007 \\ 4.053 \pm .007 \\ 4.127 \pm .007 \end{array}$	S(1), S(2) S(1), S(3) S(2), S(3) S(1), S(1) S(2), S(3)
Ag—As	2.69	Ag'' —As' Ag'' —As Ag'' —As' Ag' —As' Ag'''—As	$\begin{array}{c} 3.846 \pm .008 \\ 3.924 \pm .008 \\ 4.113 \pm .008 \\ 4.180 \pm .009 \\ 4.296 \pm .008 \end{array}$	S(1), S(2) S(1), S(2) S(1), S(2) S(2), S(3) S(1), S(2)

 Table 12. Metal-metal contact distances

1950). The distances between dissimilar metals, such as Pb-Ag and Pb-As, are only slightly greater than the sum of the metallic radii. These metal-metal interactions undoubtedly contribute to the bonding of the structure. A curious feature of the structure is indicated in Fig. 7, which presents a projection of the unit-cell contents along a. If the atoms were located in the ideal substructure positions, planes of atoms parallel to (001) would be present at $z = \frac{1}{4}$ and $z = \frac{3}{4}$. The displacements of the atoms from these positions result in alternate (010) slabs within which all bonds are either parallel to or normal to ⁶ planes close to (012) or (01 $\overline{2}$). One of these slabs is indicated by shading in Fig. 7. The Ag atoms are located at the boundary of the slabs. Ag atoms repeated by the a glide belong alternately to neighboring slabs.

⁶ The long Pb—S(3)" bond is an exception. This bond has been omitted from Fig. 7 for clarity.

The principal axes of the thermal-vibration ellipsoids are given in Table 13. The significance of these values is questionable because of the possibility of interaction between the scale factors and the temperature-factor coefficients β_{11} . The results obtained, however, bear relations to the geometry of the coordination polyhedra which are physically reasonable. The largest principal axis of thermal vibration for the Ag atom (0.225 Å) is normal to the plane of the triangular group formed by Ag and its three nearest neighbors. The other two principal axes are in the plane of this group. This triangle is not equilateral. The



Fig.7. Projection of the unit-cell contents of marrite parallel to a

intermediate vibration axis (0.176 Å) is normal to the long dimension of this group. The smallest axis (0.118 Å) is parallel to the long dimension and approximately in the direction of the Ag-S(2)' bond.

The largest principal axis of thermal vibration for the As atom is along the axis of the AsS_3 pyramid. The remaining two principal directions are normal to the axis of the pyramid. The intermediate axis (.099 Å) is approximately in a plane containing the pyramid axis and the longest As—S(1) bond. The smallest principal axis (.048 Å) is in a plane containing the pyramid axis and the second-longest As—S(3) bond.

The principal axes of thermal vibration for the Pb atom are each oriented in directions towards the centers of certain faces of the distorted coordination octahedron. Because of the distorted nature of this

Atom	Prin- cipal axis	\mathbf{Rms}	Orientation with respect to					
Atom		amplitude	a	b	с			
As	1	$.153\pm.011{ m \AA}$	$12.8^{\circ} + 6.5^{\circ}$	$95.8^{\circ} + 7.6^{\circ}$	$79.8^{\circ} + 7.8^{\circ}$			
	2	$.048 \pm .025$	$79.3^{\circ} + 6.2^{\circ}$	$31.2^{\circ} + 14.1^{\circ}$	$119.1^{\circ} + 14.4^{\circ}$			
	3	$.099 \pm .015$	$97.0^{\circ} \pm 9.2^{\circ}$	$59.5^{\circ} \pm 14.3^{\circ}$	$31.2^\circ \pm 13.8^\circ$			
	1	$0.085\pm0.007{ m \AA}$	$18.1^\circ\pm~4.3^\circ$	$88.3^{\circ} \pm 5.1^{\circ}$	$109.3^{\circ} \pm 4.1^{\circ}$			
\mathbf{Pb}	2	$.129\pm.005$	$103.6^\circ\pm~5.8^\circ$	$43.8^\circ \pm 13.0^\circ$	$130.0^{\circ}\pm12.0^{\circ}$			
	3	$.141 \pm .004$	$78.2^{\circ}\pm~5.0^{\circ}$	$46.3^{\circ} \pm 12.9^{\circ}$	$46.5^\circ\pm~11.6^\circ$			
	1	$.225\pm.008{ m \AA}$	$42.4^\circ\pm~4.7^\circ$	$130.3^{\circ} \pm 6.0^{\circ}$	$80.2^{\circ}\pm 6.2^{\circ}$			
$\mathbf{A}\mathbf{g}$	2	$.118 \pm .009$	$49.8^\circ\pm~4.3^\circ$	$53.0^\circ\pm 4.6^\circ$	$119.0^{\circ} \pm 6.4^{\circ}$			
0	3	$.176\pm.008$	$78.9^\circ\pm~6.8^\circ$	$62.1^{\circ}\pm 6.9^{\circ}$	$30.9^\circ\pm 6.6^\circ$			
	1	$ m \left .170\pm.020 m \AA ight $	$45.1^{\circ}\pm23.6^{\circ}$	$103.3^\circ\pm~14.0^\circ$	$49.1^{\circ}\pm22.3^{\circ}$			
S(1)	2	$.081\pm.038$	$87.0^\circ \pm 30.5^\circ$	$16.2^\circ\pm~27.1^\circ$	$74.2^{\circ}\pm32.8^{\circ}$			
	3	$.113 \pm .030$	$134.9^\circ\pm23.7^\circ$	$99.1^{\circ}\pm~41.3^{\circ}$	$45.1^{\circ} \pm 27.0^{\circ}$			
	1	$ m \left .064 \pm .049 m \AA ight $	$33.9^\circ \pm 36.8^\circ$	$ 103.8^{\circ} \pm 22.0^{\circ} $	$121.4^{\circ} \pm 29.9^{\circ}$			
S(2)	2	$.157 \pm .022$	$96.1^\circ\pm17.1^\circ$	$35.0^\circ\pm~21.9^\circ$	$124.1^\circ \pm 19.7^\circ$			
	3	$.113 \pm .025$	$56.8^\circ \pm 36.8^\circ$	$58.6^{\circ}\pm 24.0^{\circ}$	$50.0^{\circ}\pm~31.9^{\circ}$			
	1	$ ight $.197 \pm .023 Å	$15.1^\circ \pm 11.4^\circ$	92.7° \pm 9.5°	$76.3^{\circ} \pm 11.5^{\circ}$			
S(3)	2	$0.086\pm .032$	$83.3^\circ \pm 30.6^\circ$	$17.1^{\circ} \pm 125.0^{\circ}$	$105.7^\circ\pm123.3^\circ$			
• •	3	$.097\pm.032$	$ $ 103.5 $^{\circ}$ \pm 19.0 $^{\circ}$	$73.2^{\circ} \pm 126.8^{\circ}$	$21.1^{\circ} \pm 96.5^{\circ}$			

Table 13. Principal axes and orientations of thermal-vibration ellipsoids

polyhedron, the opposite end of each of the principal axes is directed between sulfur atoms forming an edge of the octahedron, rather than toward the center of a second face. The largest principal axis (.141 Å) is directed towards the face S(2)—S(3)'—S(3)'', and between S(1) and S(3)''. The intermediate axis (.129 Å) is directed towards the face S(1)-S(1)'-S(3)''', and between S(2) and S(3)''. The third axis (.085 Å) is directed towards the face S(1)'-S(3)''-S(3)'', and between S(1) and S(2). The edges of the octahedron towards which the principal axis of thermal vibration are directed are three of the four largest S-S contact distances in the PbS₆ octahedron.

The thermal motion of the light sulfur atoms does not permit detailed interpretation because of the large standard deviations attached to these parameters. The results of Table 13 are, for the most part, physically reasonable. The principal directions of vibration of S(1) are again directed between centers of faces of the distorted coordination octahedron and an opposite edge. The disposition of bonds about S(2) possesses an approximate symmetry plane passing through Pb, S(2) and Ag', and between Ag—As'', and As'—As'''. The thermal-vibration ellipsoid conforms to this pseudosymmetry. Two principal directions (.157 and .064 Å) lie in the plane Pb—S(2)—Ag' as might be expected.

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