THE CRYSTAL CHEMISTRY OF THE HOMOLOGOUS SERIES

$Pb_{3+2n}Sb_8S_{15+2n}$ (THE PLAGIONITE GROUP)

by

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Abstract

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The plagionite group consists of four minerals, fülöppite ($Pb_3Sb_8S_{15}$), plagionite ($Pb_5Sb_8S_{17}$), heteromorphite ($Pb_7Sb_8S_{19}$), and semseyite ($Pb_9Sb_8S_{21}$), which form an homologous series. Two lattice constants remain essentially invariant throughout the series, while the third increases uniformly as the Pb content increases. Semseyite, whose crystal structure was determined in detail in this work, is monoclinic, space group C 2/c with a=13.603(3), b=11.936(8), c=24.435(7) A°, β=106.047(10)°, ρ(meas.)= 6.03 gcm⁻³ and ρ(cal)=6.12 gcm⁻³ for Z=4. Intensity data was recorded both with a four-circle counter diffractometer and photographically by equi-inclination Weissenberg films. The structure was solved with the symbolic addition procedure and refined by least-squares techniques to R=10.0% for 1827 observable reflections. The asymmetric unit contains 20 atoms. Two Pb atoms are coordinated by six S atoms, one Pb atom by five S atoms and one Pb atom by seven S atoms in octahedral-like configuration. A fifth Pb atom has an irregular 8-fold coordination which may be described as a square antiprism. Three of the four independent Sb atoms have square pyramidal coordination; a fourth forms a trigonal pyramidal group. Of the eleven independent S atoms, five have octahedral-like configuration, five tetrahedral and one square-pyramidal. The structure is composed of slabs of PbS-like structure which run parallel to (112) and ($\overline{1}1\overline{2}$) alternately along c and extend indefinitely along [$\overline{1}$10] and [110] respectively.

From study of the structures of plagionite and semseyite a model was created which could predict the structures of heteromorphite and fülöppite, in projection. The model involves two types of addition of Pb at a previously Sb site. The interaxial angle β is correctly predicted as well as the change in c sin β and the density increase. An extension of the plagionite group past semseyite is predicted as possible synthetic materials.

Thesis Supervisor: Bernhardt John Wuensch

Title: Associate Professor of Ceramics

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indebted to the members of the "Wuensch" group, past and present, who helped her weather the many storms of a structure determination.

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Chapter 1

Prologue

In this era of pragmatism and practicality man is pressed to justify his actions. Such is the case for the layman and the scientist. The scientific community thinks, not altogether unwillingly, in terms of marketability. They offer apologia for their heritage, neglecting the dictum of their very name, scire - to know.

This thesis does not concede its dignity to the idols of profits and patentability. The minerals of the plagionite group will probably never be of industrial significance. Their study, however, contributes to a most practical goal - the extension of the knowledge of matter. Without such basic extensions man's world of gadgetry would not have been built.

Chapter 11

Introduction

Sulfur is one of the most prevalent compounds of our envi-
ronment. Much of the organic facet of the chemistry of sulfur
and many of its simpler inorganic compounds have been thoroughly
detailed and studied. However, the more complex inorganic com-
pounds with their potential for solid state innovation have not
been exhaustively catalogued, much less completely studied. One
of the most complicated sulfide families to suffer this lack of
attention is the sulfosalt group.

Sulfosalts are minerals characterized by the combination of
one or more metal atoms with sulfur and a Group V element such
as As, Sb, or Bi. Their compositions may be formalized as
$X_mZ_nS_p$, with Z the Group V element and X usually being Pb, Ag,
Cu, and occasionally a transition metal Zn or Hg. The integers,
m, n, and p, frequently bear no simple relationship among them-
selves, and large numbers of intermediate compounds exist in a
given pseudo-binary system (e.g. 18 in PbS - Sb_2S_3).

Of the 150 of these minerals described in the literature,
fewer than a quarter have been structurally analyzed. The results
of these analyses seriously question the adequacy of the simple
crystal chemical models usually used to predict structure.
Bonding description is no longer a simple question of isolating
first and second nearest neighbors. In the sulfosalt compounds
the sulfur coordination of the metal atoms form almost a continuum

rather than discrete neighbors. Such is the case for Bi - coordination in aikinite (2.663, 2.734. 2.996, 3.117. 3.531 A°) and Bi(4) in gladite (2.61, 2.83, 2.99, 3.49 A°) for example. (Kohatsu, I., 1971) Coordination polyhedra are frequently distorted from ideal goemetric configurations. The sulfur coordination of a given metal is often not unique; Sb for example can be three -, four -, or five-coordinated by S. Two different coordination schemes may even occur in a single compound (e.g. Sb_2S_3). (Nowacki, 1971) Such idiosyncrasies as these can not be predicted by the same crystal chemical theories that so well handle the structural and bonding properties of sulfur's fellow group member, oxygen. Thus much needs to be studied and more structural data gathered to complete the picture for sulfur.

Complete characterization of the sulfosalt compounds is hampered by inherent material difficulties. X-ray analysis is initially hindered by the scarcity of material suitable for study. Many of the minerals are rare with only a few (1 or 2) known crystals available for study. Even certain common minerals occur as twins, intergrowths, or bundles of fibers, making them unsuitable for single crystal work. Synthesis of these compounds would be an alternative. However, such work has usually been unsuccessful. The exact composition of many of the compounds is still in question making synthesis difficult. Moreover, minute traces of metals, apparently minor constituents in the sulfosalts, are usually found. Whether these are merely impurities or are required to

stabilize a mineral phase has not been conclusively ascertained in most cases. For example, Hall (1967) found that polybasite, $Ag_{16}As_2S_{11}$, was stable only when 3.1 - 7.6 wt. per cent Cu is present. The task is further complicated by the fact that the sulfosalts are low temperature phases and reactions are difficult both to initiate and to carry to completion. When synthesis proceeds with a small measure of success, the result is usually a multiphase mixture rather than good single crystals. Thus while artificially manufacturing the desired mineral is theoretically a good means of relieving the scarcity of suitable material, it has not reached the stage where it is a practical solution. X-ray analysis of the sulfosalts is still limited by the discovery of good single crystals of naturally-occuring minerals.

After this initial barrier is overcome, the solution and subsequent refinement of the sulfosalt structures is hampered by the high x-ray absorptivity of the materials. Many of these minerals contain large amounts of Pb and/or Bi - both having high mass absorption coefficients. Values up to 1500 cm^{-1} are not uncommon for Pb sulfosalts in Cu K_α x-radiation. The effect of the presence of these metals is to absorb portions of the incident and scattered x-ray beams, consequently weakening them. The depletion of intensity can be four or five orders of magnitude even for minute (10^{-2} cm) sample sizes. Correction for this effect requires an extremely accurate description of the crystal shape. On the other hand, a very small crystal must be selected to minimize the

effect. Thus the precise description of the intricate crystal shape has become most difficult. Consequences of improper correction for absorption are severe for these highly absorbing materials. The R-value, the residual error, an indicator of the correctness of the proposed structure, is in these instances limited by the absorption correction. Failure to make an accurate correction limits the preciseness of the data, which in turn limits one's ability to precisely determine the coordinates of atoms in the structure. In the case of Pb - or Bi - containing sulfosalts, the locating of the "electronically weak" sulfur is particularly difficult. Such a problem is comparable to the one faced by organic crystallographers in locating hydrogen positions. Even if the correction would be exact, the intensity data are weak due to absorption and the relative standard deviations due to counting statistics are large. This also limits the preciseness of the determination. Poor absorption correction also limits the precision with which bond distances may be measured. In Pb-Bi sulfosalts this is especially critical since both Pb and Bi have similar scattering powers and may be identified only by their coordination geometry. Imprecise correction for absorption can also appear as anomalous anisotropic thermal motion of the atoms. The detection of such real thermal motion is of importance in discussing bonding characteristics and a pseudo-effect can lead to confusing and often wrong interpretation.

Due to these inherent difficulties little is known of sulfo-

salt crystal chemistry. The study of a Pb-Sb sulfosalt group
was therefore undertaken. Eighteen minerals are known in the
Pb - Sb - S system compared with only nine in the companion
Pb- As - S system. (Table 1) All but one of the arsenic structures
are known. Only one Sb-structure, plagionite $Pb_5Sb_8S_{17}$ (Cho,
1969) is known; however, two others, zinkenite $Pb_6Sb_{14}S_{27}$ (Takeda,
1971,Takeda,1964) and boulangerite (Born and Hellner,1960),
$Pb_5Sb_4S_{11}$, have been partially determined. Among the sulfanti-
monides and sulfarsenides isostructuralism and solid substitution
are often common. However, in the Pb-Sb-S and Pb-As-S systems,
isostructuralism is seen not to be prevalent; no doubt because of
the difference in relative sizes of the As and Sb coordination
polyhedra with respect to the Pb polyhedron. Limited As sub-
stitution is still possible. (Table 1)

Due to the paucity of data much is uncertain about the poly-
hedral coordination of Sb by S in the prescence of Pb. Arsenic
in similar environments invariably assumes a trigonal pyramidal
configuration, while bismuth, the other commonly occuring Group
V element, invariably has a square pyramid of five sulfurs in a
[1+2+2] arrangement. Antimony is known to assume both coor-
dinations and can do so in a single structure, stibnite (Sb_2S_3).
Therefore, more information is needed to interpret correctly
the widely varying number of phases in the two systems.

More interestingly than merely amassing structural data,
semseyite $Pb_9Sb_8S_{21}$, the subject of the current work, has pro-

TABLE   1

Comparison of Pb-As-S System with Pb-Sb-S System

Reduced Composition Pb_xMyS		PbS-As_2S_3 Mineral	PbS-Sb_2S_3 Mineral
.600	.267	gratonite $Pb_9As_4S_{15}$ (1,2)	
.565	.304	jordanite $Pb_{13}As_7S_{23}$(?) (3)	gercronite $Pb_{13}(Sb,As)_8S_{23}$
.500	.333		falkmanite $Pb_3Sb_2S_6$
.454	.363		boulangerite $Pb_5Sb_4S_{11}$(?) (4)
.444	.370		sterryite $Pb_{12}(Sb,As)_{10}S_{27}$ (?)
.429	.381		semseyite $Pb_9Sb_8S_{21}$
.425	.550		sorbyite $Pb_{17}(Sb,As)_{22}S_{40}$ (?)
.415	.390		madocite $Pb_{17}Sb_{16}S_{41}$(?)
.400	.400	dufrenoysite $Pb_2As_2S_5$ (5)	veenite $Pb_2(Sb,As)_2S_5$
.379	.414		dadsonite $Pb_{11}Sb_{12}S_{29}$

Table 1
(continued)

Comparison of Pb-As-S System with Pb-Sb-S System

Reduced Composition Pb_xMyS		$PbS-As_2S_3$ Mineral	$PbS-Sb_2S_3$ Mineral
.372	.419		playfairite $Pb_{16}Sb_{18}S_{43}$ (?)
.368	.421		heteromorphite $Pb_7Sb_8S_{19}$
.361	.426		launayite $Pb_{22}Sb_{26}S_{61}$ (?)
.350	.450	rathite Ia $Pb_9As_{13}S_{28}$ (6)	
.322	.456	rathite II $Pb_9As_{13}S_{28}$	
.306	.473	acentric baumhauerite $Pb_{11}As_{17}S_{36}$ (7)	
.300	.500	rathite I $(Pb,Tl)_3As_5S_{10}$ (8)	
.300	.500	rathite III $Pb_3As_5S_{10}$ (9)	
.294	.491		plagionite $Pb_5Sb_8S_{17}$ (10)
.280	.480		robinsonite $Pb_7Sb_{12}S_{25}$ (?)

Table 1
(continued)

Comparison of Pb-As-S System with Pb-Sb-S System

Reduced Composition Pb_xMyS		$PbS-As_2S_3$ Mineral	$PbS-Sb_2S_3$ Mineral
.278	.500	centric baumhauerite $Pb_5As_9S_{18}$	
.273	.485		guettardite $Pb_9(Sb,As)_{16}S_{33}$ (?)
.250	.500	scleroclase $PbAs_2S_4$ (11)	twinnite $Pb(Sb,As)_2S_4$
.222	.519		zinkenite $Pb_6Sb_{14}S_{27}$ (?) (13,12)
.222	.556	hutchinsonite $(Pb,Tl)_2As_5S_9$ (14)	
.200	.553		fülöppite $Pb_3Sb_8S_{15}$

TABLE 1
continued

(1)   Rosch (1963)
(2)   Ribar and Nowacki (1969)
(3)   Wuensch and Nowacki (1966)
(4)   Born and Hellner (1960)
(5)   Marumo and Nowacki (1967)
(6)   LeBihan (1962)
(7)   Engel and Nowacki (1969)
(8)   LeBihan (1962)
(9)   LeBihan (1962)
(10) Wuensch and Cho (1970)
(11)   Iitaka and Nowacki (1961)
(12) Takeda and Sadanaga (1964)
(13) Takeda and Sadanaga (1964)
(14) Takeuchi (1965)

posed structural relationships with the one known structure, plagionite $Pb_5Sb_8S_{17}$. It has been suggested that fülöppite $Pb_3Sb_8S_{15}$, plagionite, heteromorphite $Pb_7Sb_8S_{19}$, and semseyite form an homologous series. It may be characterized as $Pb_{3+n}Sb_8S_{15+n}$ with n=0 (fülöppite) to n=3 (semseyite). Two of the lattice constants, a and b, remain essentially invariant while the third, c, increases uniformily with n. (Table 2) Jambor (1969) has shown that the volume and the densities (both measured and calculated) increase uniformly with n. (Figure 1) He also points out that (c sin β) increases more uniformly than c as n increases. The probable space group for all the members of the series is C2/c with Z=4. As one proceeds from fülöppite to semseyite, one observes an increasingly perfect ´{112} cleavage.

Not only do the minerals of the plagionite group show similar characteristics, but as a group they are likewise dissimilar from the other Pb-Sb sulfosalts. The plagionite minerals occur as tabular, lozenge-like crystals rather than fibrous needles as do most other Pb-Sb sulfosalts. The plagionite group minerals do not exhibit the common **4** A° (or multiple) translation indicative of the direction of a stibnite-like chain as do many Sb and all Bi sulfosalts. Lastly they have no As analogues, nor do they permit As substitution although both of these traits are not uncommon in the Sb sulfosalts. Thus it appears that relationships must exist among the structures of these four minerals. If the

TABLE 2

Cell Dimensions of the Plagionite Group

	a	b	c	β	c sin β
Fülöppite	13.41 Å	11.71	16.90	94°43'	16.8 Å
Plagionite	13.49	11.87	19.98	107°10'	19.1 Å
Heteromorphite	13.60	11.93	21.22	90°50'	21.2 Å
Semseyite	13.60	11.94	24.45	106°2'	23.5 Å

(after Jambor (1969))

FIGURE 1

Density Variation in the Plagionite Group
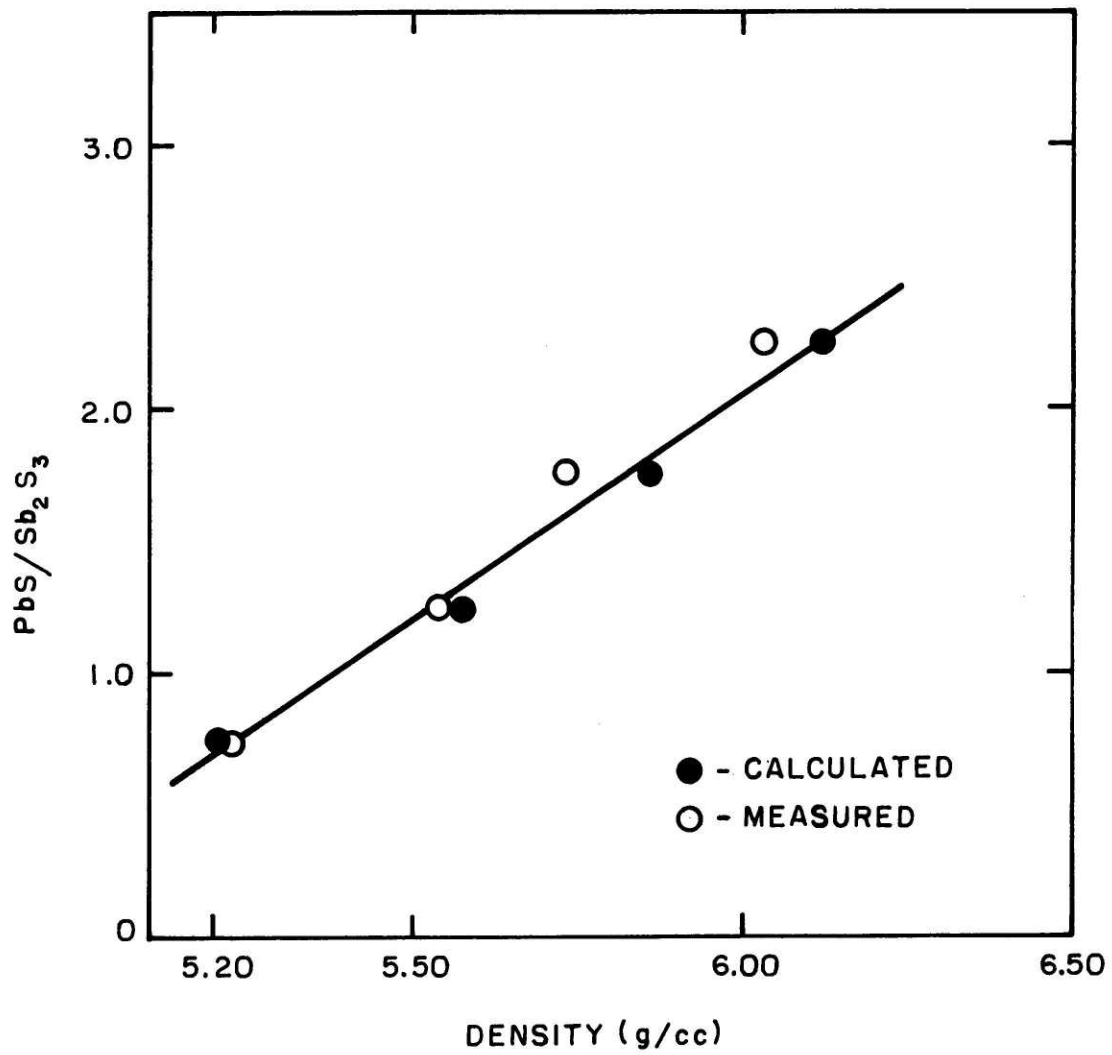
FIGURE 1

continued

Volume Variation of the Plagionite Group
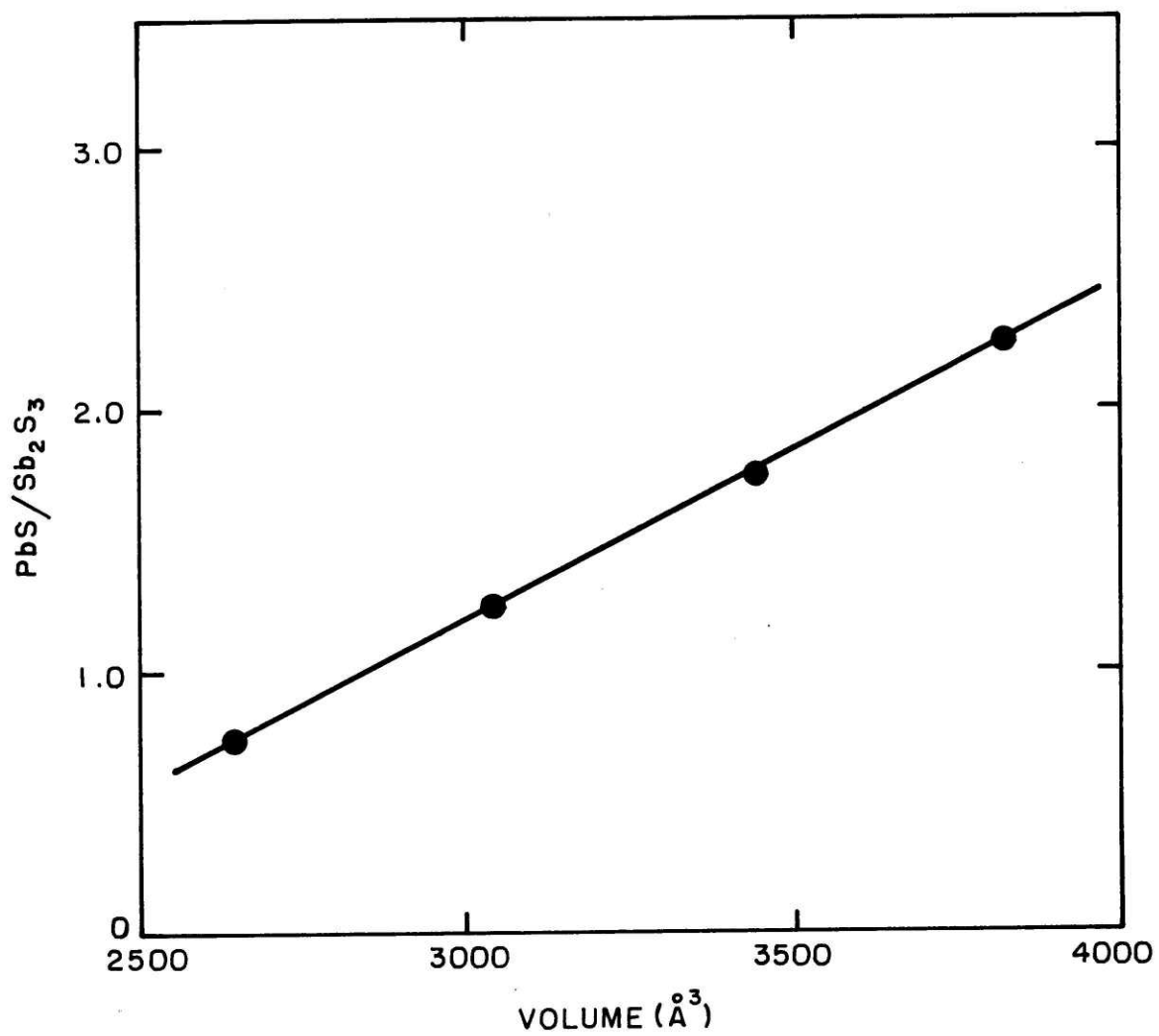
basis of the homology can be established, then useful generali-
zations on structure may be made for the whole series, such as
those made in the V_nO_{2n-1} $(3 < n < 8)$ and Ti_nO_{2n-1} homologous
series. (Horiuchi, 1972)

Chapter III

The Experimental Work

A.   Preliminary X-ray Analysis

Semseyite, $Pb_9Sb_8S_{21}$, is the final and most complicated member of the plagionite group. Previously Peacock and Nuffield (1945) studied semseyite but they compiled mineralogical data but no structural data. They report that crystals of the material are somewhat lighter in color than plagionite with freshly broken surfaces showing nearly tin-white with a good metallic luster. The measured specific gravity for their crystals was 6.03.

The crystal used in this investigation was from Kisbanya, Roumania (Harvard Museum catalogue #99697). Due to the high x-ray absorptivity (μ_ℓ = 1304.74 cm^{-1} for CuKα) an attempt was made to grind a sphere from the material following the method of Bond (1951). Difficulty was encountered as semseyite exhibits a perfect {112} cleavage. A slightly ellipsoidal crystal was finally prepared for study. The average radius for the crystal was 0.00873 cm and $\mu_\ell r$ = 11.391 for Cu Kα.

Preliminary x-ray work indicated that semseyite was monoclinic with diffraction symmetry 2/m. The second setting (b - axis unique) was selected for reference of the lattice constants. Systematic extinction, h + k $\neq$ 2n for hkℓ and $\ell \neq$ 2n for 00ℓ, indicated that space groups C 2/c and C c were permitted. This is consistent with the diffraction symbol 2/mC_/c. The centro-symmetric space group C 2/c (C_{2h}^6) was chosen for subsequent study based on a previous morphological study. (Peacock and

Nuffield, 1945). This choice was subsequently confirmed by
statistical tests on the set of diffracted intensities.

Precision lattice constants were measured with the aid of
data collected with a back-reflection Weissenberg camera (dia-
meter = 114.592 mm) and Cu radiation. With two settings of the
crystal (b axis and c axis parallel to the spindle axis), 130
observations were indexed and film spacings measured. Precision
lattice constants were obtained with a least-squares fit of the
data by the use of Burnham's computer program LCLSQ (1961). Cor-
rections were made for sample absorption, camera eccentricity,
and film shrinkage. The lattice constants thus obtained were:

$$a = 13.603 \pm .003 \text{ A}° \qquad \alpha = 90.0°$$
$$b = 11.935 \pm .007 \qquad \beta = 106.046 \pm .010$$
$$c = 24.452 \pm .007 \qquad \gamma = 90.0 .$$

The resulting cell volume is 3815.7 $\text{A}°^3$ with a calculated density
of 6.12. This density assumes 4 formula weights per unit cell.
Thus the cell contents are $Pb_{36}Sb_{32}S_{84}$, a total of 152 atoms. The
calculated density of 6.12 compares favorably with the measured
value of Peacock and Nuffield (1945) of 6.03. The lattice constants
and the direct lattice correlation matrix as well as the constants
of Peacock and Nuffield are presented in Table 3.

B. The Data Collection

During the determination of the space group with the pre-
cession camera and Mo radiation and the lattice constants determi-
nation, it was noted that the magnitude of the reflected inten-

TABLE 3

Semseyite Lattice Constants

Present Work	Peacock & Nuffield (1945)

	Present Work	Peacock & Nuffield (1945)
a	13.60 3 (3) Å	13.61 Å
b	11.93 6 (8)	11.99
c	24.45 3 (7)	24.52
α	90°	90°
β	106.047°(10)	105°49'
γ	90°	90°

Direct Lattice Correlation Matrix

	a	b	c	α	β	γ
a	1.0	.610	.567	0.0	-.238	0.0
b		1.0	.302	0.0	-.002	0.0
c			1.0	0.0	-.427	0.0
α				1.0	0.0	0.0
β					1.0	0.0
γ						1.0

sities was low. Peak to background ratios were also very small.
Both of these problems were caused by the smallness of the cry-
stal and the large x-ray absorptivity. Since neither predicament
augered well for the planned data collection with Mo Kα radiation
by film methods, it was decided to attempt to use monochromated
Ag radiation. The monochromation would improve the peak to back-
ground ratio and the absorptivity for Ag (252.1 cm^{-1}) was much
lower than that for Cu (1304.74 cm^{-1}). A Supper monochromator
was used with both the precession and equi-inclination Weissen-
berg cameras. Unfortunately scattering from the small crystal
proved so weak that the data collection times would be prohibi-
tive. Thus it was decided to utilize Cu Kα radiation and the
Weissenberg camera (to minimize the crystal to film distance).
A highly accurate absorption correction was necessitated.

The initial data for semseyite were collected with a three-
film pack on an equi-inclination Weissenberg camera. Eight levels,
h0ℓ to h7ℓ , were collected with exposure times ranging from 96
hours (h0ℓ) to 225 hours (h7ℓ). The films were then scanned by
an autophotodensitometer unit at Boston University.* The optical
density of the film was reported at 100μ intervals both hori-
zontally and vertically. The data were stored on magnetic tapes
by the Optronics unit.

C.   Initial Data Analysis

The individual optical densities were reconstructed into

_____
*PHOTOSCAN system P-1000 is manufactured by OPTRONICS INTERNA-
TIONAL INC.,Chelmsford, Massachusetts.

reflection intensities by the use of the computer program INTEN
(initially written by R.Kadlec (Boston University) and subsequent-
ly modified by I. Kohatsu (1971)). Two major methods were
utilized in a later version of the program modified by the author.
(Appendix C) The first method involved extracting and assembling
around each reflection a "window" sufficiently large to include
the peak and ample background but small enough not to include
any other reflection. The second alternative was to reconstruct
the whole film by "dumping" the stored densities in the same order
in which they were recorded. Then the whole digitized record of
the film could be graphically indexed much as a normal x-ray
film is indexed. Although the methods provided integrated inten-
sities, both were tedious and neither completely satisfactory.
(See Appendix A.) Reflections which were undiscernable to the
eye on the x-ray film were marked unobservable and subsequently
excluded from initial structure refinement.

Of the nearly 1500 integrated intensities measured, over
one-third were marked unobservable. The remainder (approximately
1000) were corrected for Lorentz and polarization effects as well
as absorption. The author followed the method of Prewitt and
Wuensch (1965) and utilized the program ACAC which she extensively
modified to permit the use of the Gaussian quadrature method.
As mentioned in the Introduction, the absorption-effect correction
is extremely critical for this material. Therefore, the crystal
shape was carefully measured. The small crystal is an ellipsoid
of circular cross-section described mathematically as

$$\frac{x^2}{a^2} + \frac{y^2 + z^2}{b^2} = 1$$ with a = 0.00794 ±.0003 cm and b = 0.00952 ± .0003 cm. The calculated volume of the sample, using 512 integration points, was 0.2516 x 10^{-5} cm^3 . The calculated geometrical volume was 0.3014 x 10^{-5} cm^3 . Three attempts at the absorption correction were made varying ellipsoid size and orientation. The best and final try yielded agreement of 14% between equivalent $F_{hk\ell}$'s. Much of the error was attributed to inaccuracies in the original measurement of the intensities.

Chapter IV

Initial Structure Determination

The essential job facing a crystallographer in analyzing a large structure is the determination of the phases of the structure factors. For a centrosymmetric structure this amounts to the assignment of positive or negative signs to the magnitude of the structure factors. The structure factor, which carries the atomic position information, is a complex quantity but only the magnitude (i.e. the reflection intensity) can be measured with current techniques. There are two main solutions to this dilemma - the Patterson method (Buerger, 1959) and Symbolic Addition (Karle and Hauptmann, 1953).

The Patterson method involves looking into atom-atom interactions in Patterson space. The Patterson function at the point (u,v,w) represents the average product of the electron density at points (X,Y,Z) and $(X+u,Y+v,Z+w)$. Therefore when atoms sit at the two points, the function will have maxima. Thus interatomic vectors may be obtained. It should be noted that since u,v,w cover all space, $n(n-1)$ peaks will result from the interactions of n atoms. Structures containing small numbers (1,2,or 3) of high atomic-number atoms and the rest electronically light atoms are particularly well suited to this method. Since the heavy atoms determine most of the phases, the positions of the lighter atoms can be determined with the regular electron density synthesis.

However, if the crystal structure contains large numbers of
heavy and moderately heavy atoms and atomic arrangement is com-
plicated, a Patterson map is nearly impossible to interpret. If
the arrangement of atoms can be said to approach randomness, then
the method of symbolic addition can be used. With this method
only n peaks versus n(n-1) peaks will appear in the same volume
using electron density techniques. The symbolic addition method
depends on inequalities that exist between structure factors with
certain sets of hkℓ's. (Karle and Hauptmann, 1953; Sayre, 1952)
For a further discussion of the symbolic addition method, see
Appendix B. Thus if enough data is examined, phases can be de-
termined probalistically.

Since the structure of semseyite contains five independent
Pb's and four Sb's and is complicated, the Patterson method was
discarded in favor of symbolic addition. The raw data (corrected
for absorption, Lorentz, and polarization effects) were scaled
so that all 'k' levels were on the same basis. The structure
factors were multiplied by

$$\frac{\text{Exposure time of the } k^{th} \text{ level}}{\text{Exposure time of the } h0\ell \text{ level}}^{-0.5}.$$

This data was then processed by the program FAME (Fortran Auto-
matic Manufacture of E's)(Dewar and Stone). The three hundred
largest $F_{hk\ell}$'s which were measured were converted to $E_{hk\ell}$'s, the
normalized structure factors - $F_{hk\ell} / \Sigma f_i$ where f_i are the
atomic scattering factors. The best set of $E_{hk\ell}$'s selected on the

basis of absolute magnitude and number of interactions with other hkℓ's were assigned symbolic signs A through H. The results of the Wilson calculation in FAME yielded an overall scale factor of 0.4954 (to convert from arbitrary to electron units) and a temperature factor (β) of 0.6813. The statistical distribution of $E_{hkℓ}$'s (derived from FAME) indicated a centric structure (Table 4). The symbolic signs assigned to the eight initial reflections are given in Table 5.

The normalized structure factors ($E_{hkℓ}$'s) were used as input to MAGIC (Multiphase Automatic Generation from Intensities in Centric Crystals)(Dewar and Stone). The eight reflections were used to initialize MAGIC. Through twenty successive iterations of MAGIC increasing numbers of real (+ or -) signs were acquired. Ultimately 249 $E_{hkℓ}$'s were signed, out of the possible 300 reflections. The sign combinations and the contradiction indices are given in Table 6. Of the four most probable sign combinations, two showed extremely low contradiction indices while the other two were slightly higher. All remaining sign combinations exhibited large contradiction indices.

The phased $E_{hkℓ}$'s (based on the four most probable sign combinations) were then used as input to an electron density synthesis program, FORDAP - 2 (Zalkin) to provide four E-maps. The Pb and Sb positions were readily located and used in an initial least-squares refinement using the program SFLS-5 (Prewitt, 1962). The first and third combinations yielded arrangements

TABLE 4

Statistical Distribution of E's Calculated from Wilson Plot

Quantity	Calculated	Theoretical (Centric)	Theoretical (Acentric)
Average Mag of E's	0.805	0.798	0.886
Average of E^2	1.023	1.000	1.000
Average of $|E^2-1|$	1.039	0.968	0.736
Percentage Greater Than One	27.94	32.00	37.00
Percentage Greater Than Two	6.16	5.00	1.80
Percentage Greater Than Three	0.33	0.30	0.01

TABLE   5

Assignment of Symbolic Signs

h	k	ℓ	E	Sign
2	-5	2	2.6760	A
6	-6	1	3.0430	B
-5	-5	5	2.7280	C
-2	-6	2	2.6440	D
-4	-11	4	3.4800	E
-3	-6	1	2.4100	F
3	-5	5	2.8180	G
-8	-16	2	2.8090	H

TABLE   6

Sign Combinations and Contradiction Indices

Symbols								Contradiction
A	B	C	D	E	F	G	H	Index
+	+	0	+	0	+	+	−	63.1
−	+	0	−	0	+	+	+	72.9
+	−	0	−	0	−	+	−	108.0
−	−	0	+	0	−	+	+	127.6
+	−	0	−	0	+	+	−	1349.7
−	−	0	+	0	+	+	+	1357.3
+	+	0	+	0	−	+	−	1371.8
−	+	0	−	0	−	+	+	1396.1
−	−	0	+	0	−	+	−	1718.7
+	+	0	+	0	+	+	+	1752.7
+	−	0	−	0	−	+	+	1755.1
−	+	0	−	0	+	+	−	1764.4
−	+	0	−	0	−	+	−	1955.5
−	−	0	+	0	+	+	−	1963.5
+	+	0	+	0	−	+	+	1964.7
+	−	0	−	0	+	+	+	1994.4
+	+	0	+	0	+	−	+	2526.3
−	+	0	−	0	+	−	−	2539.0
+	−	0	−	0	−	−	+	2553.0
−	−	0	+	0	−	−	−	2577.3
+	−	0	−	0	+	−	+	2887.1
−	−	0	+	0	+	−	−	2892.2
+	+	0	+	0	−	−	+	2913.3
−	+	0	−	0	−	−	−	2933.1
+	+	0	+	0	−	−	−	3349.1
−	+	0	−	0	−	−	+	3349.1
−	−	0	+	0	+	−	+	3381.7
+	−	0	−	0	+	−	−	3392.0
−	−	0	+	0	−	−	+	3644.0
+	+	0	+	0	+	−	−	3678.0
−	+	0	−	0	+	−	+	3678.8
+	−	0	−	0	−	−	−	3679.8
+	+	0	−	0	−	+	+	8242.3
−	+	0	+	0	−	+	−	8246.8
+	−	0	+	0	+	+	+	8263.3
−	−	0	−	0	+	+	−	8285.6
+	−	0	+	0	−	+	+	8498.6
−	−	0	−	0	−	+	−	8530.3
−	+	0	+	0	+	+	−	8535.9
+	+	0	−	0	+	+	+	8538.9
−	+	0	+	0	+	+	+	8622.3
+	+	0	−	0	+	+	−	8646.8
+	−	0	+	0	−	+	−	8651.0

TABLE 6
(continued)

Sign Combinations and Contradiction Indices

		Symbols						Contradiction
A	B	C	D	E	F	G	H	Index
−	−	0	−	0	−	+	+	8653.0
+	−	0	+	0	+	+	−	8842.7
−	+	0	+	0	−	+	+	8849.9
−	−	0	−	0	+	+	+	8861.0
+	+	0	−	0	−	+	−	8874.7
+	+	0	−	0	−	−	−	9746.1
−	+	0	+	0	−	−	+	9759.7
+	−	0	+	0	+	−	−	9766.0
−	−	0	−	0	+	−	+	9795.5
+	−	0	+	0	−	−	−	10179.7
−	−	0	−	0	−	−	+	10198.7
−	+	0	+	0	+	−	+	10208.3
+	+	0	−	0	+	−	−	10222.1
−	+	0	+	0	−	−	−	10467.8
+	−	0	+	0	+	−	+	10468.5
−	−	0	−	0	+	−	−	10471.0
+	+	0	−	0	−	−	+	10497.2
−	+	0	+	0	+	−	−	10541.8
+	+	0	−	0	+	−	+	10563.4
−	−	0	−	0	−	−	−	10563.9
+	−	0	+	0	−	−	+	10570.5

which did not refine. The second combination initially refined
to an R value of 29% without the sulfur atoms. However, upon
addition of the sulfurs (located on a difference Fourier map),
no atomic arrangement could be found that yielded believable
(i.e. not too short) interatomic distances. The fourth sign
group refined equally well and yielded nine good sulfur positions
with reasonable interatomic distances. The E-map derived from
this sign group is given in Figure 2 for the metal positions only.
Although initially there was some ambiguity as to the iden-
tification of some Sb and Pb, this was later resolved by
difference-Fourier synthesis maps. The atomic configuration
ultimately refined to a R_{reject}= 18.9% (omitting rejected reflec-
tions). This refinement included anomalous scattering, isotropic
temperature factors, and rejection of all $F_{hk\ell}$'s with (F_{cal} -
F_{obs})/F_{obs} greater than 75%. The atomic parameters are given in
Table 7.

On the whole, the atomic arrangement seemed reasonable,
however, there were puzzling elements. Two of the eleven sulfurs
were unlocatable - unusual for even a relatively light atom in
a correct structure. With a very reasonable and loose rejection
criteria ($\Delta F/F$> 75%) over one-third of the data were rejected -
unreasonable with a correct structure and a good set of data.
These troublesome factors forced the author to conclude that
collection of another set of data was in order. It was decided

FIGURE 2

Composite E-map
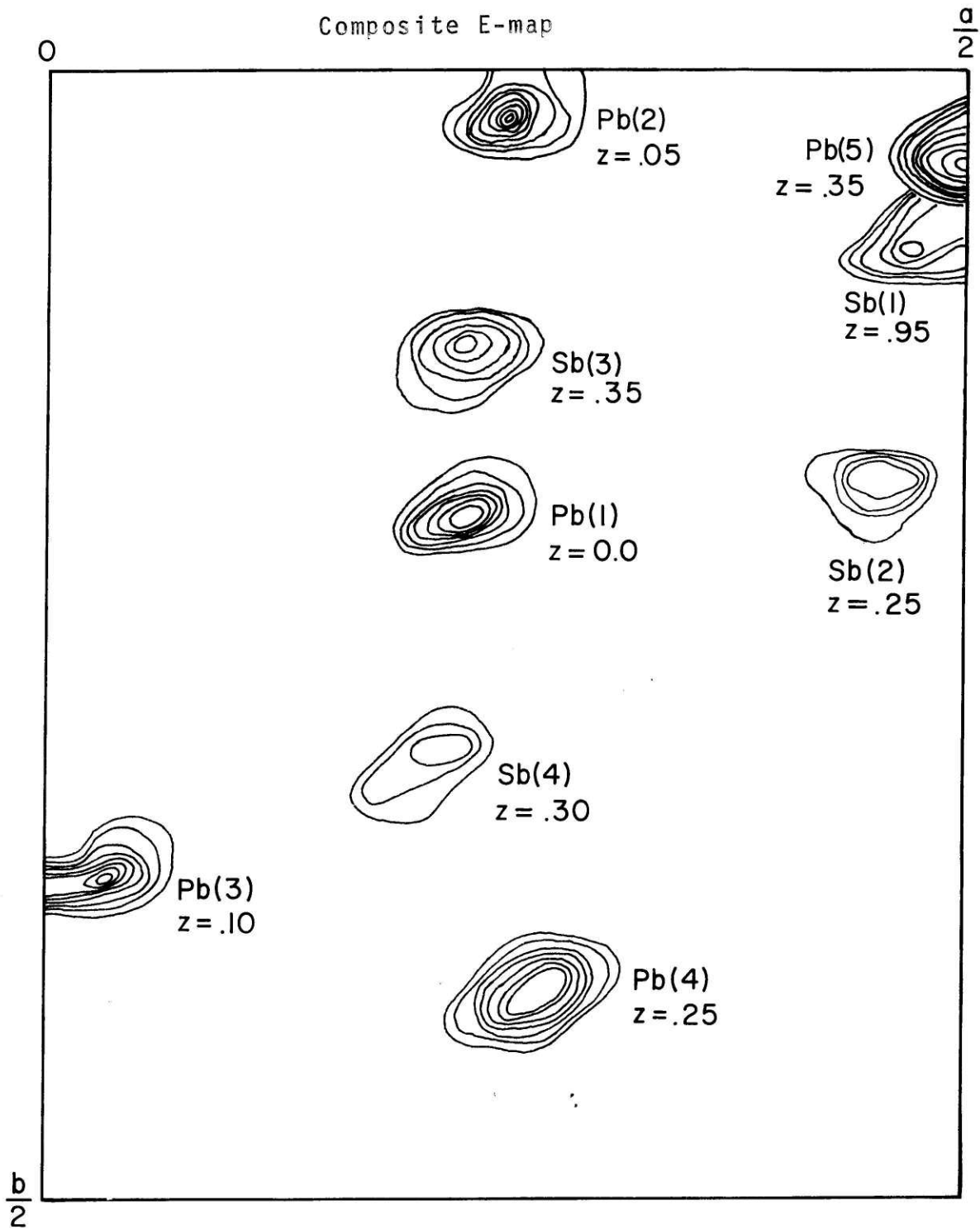
TABLE   7

Atomic Parameters Initial Refinement

	Sb(1)	Sb(2)	Sb(3)	Sb(4)	
x	.4825	.4528	.2248	.5069	
y	.9440	.2620	.3216	.3319	
z	.9257	.8157	.8779	.9742	
β	.8817	.9053	.7311	1.0578	

	Pb(1)	Pb(2)	Pb(3)	Pb(4)	Pb(5)
x	.2249	.2502	.0231	.2684	.50
y	.0130	.0547	.1141	.2256	.0404
z	.8076	.9826	.6426	.5935	.25
β	1.1372	1.5389	1.0207	1.1619	1.2639

	S(1)	S(2)	S(3)	S(4)	S(5)
x	.00	.3772	.3839	.3575	.3884
y	.0972	.1702	.0146	.1681	.2774
z	.25	.3492	.1307	.4988	.1932
β	.7432	1.1616	.0001	1.7254	2.4989

	S(6)	S(7)	S(8)	S(9)
x	.1400	.1717	.3838	.1280
y	.3519	.1048	.4430	.0686
z	.2565	.1802	.4506	.3989
β	.4129	2.9008	1.0911	.0001

to collect this set with the same crystal on a four-circle auto-
mated diffractometer with monochromated Mo radiation. Thus
absorption effects would be reduced and the inaccuracies of film
scanning avoided.

Chapter V

Structure Refinement with new Data

New data was gathered for semseyite on a Picker-automated four-circle diffractometer in Dr. Charles T. Prewitt's laboratory at the State University of New York at Stony Brook. 2125 reflection intensities were collected in nearly four days using graphite-monochromated Mo Kα radiation. This data set duplicated the one taken earlier with film methods and Cu Kα. The data was integrated and corrected for Lorentz and polarization effects during the collection process. The resulting structure factors were then corrected for absorption by the author in the manner previously described. (See Chapter III.) Agreement between 24 sets of equivalent structure factors was 6% compared with 14% for the first data set. Agreement was compared by calculating $(F_1 - F_2)/(.5(F_1+F_2)$ for each equivalent pair. Identical corrections were applied in each case.

Since the previous data set had refined to 18.9%, it was assumed that the metal positions were essentially correct. Thus these positions were used to initialize the refinement process. After one cycle of refining only the scale factor (initialized at 1.0) and two subsequent cycles of refining both atomic coordinates of the nine metals and the scale factor, the discrepancy index was 21.6%. This indicated that the hypothesis on the metal positions was correct. An electron difference Fourier synthesis was constructed. The positions of the eleven sulfur atoms were readily

located. Comparison with the original data set indicated that only six of the nine original sulfur positions agreed with the present data set. Table 8 compares the metal atomic positions of the two data sets.

Upon location of the sulfur atoms, they were included in the least-squares refinement and allowance was made for anomalous dispersion. Four cycles of refinement were performed in which the scale factor and atomic positions were varied. At this juncture the R value, defined as $(\Sigma||F_{obs}|-|F_{cal}||)/\Sigma F_{obs}$, was 12.1% indicative of a correct structure. Another difference Fourier synthesis was performed, using the data phased on the current refinement. No large anomalous peaks were discovered. Anisotropic thermal motion was suggested, however, for the metal atoms.

At this point the isotropic temperature factors of all the metal and sulfur atoms were allowed to vary from their previously fixed values of 1.0 A°². After six cycles of refinement, the unweighted R value was 10.6% while the R weighted by sigma from counting statistics, $R = (\Sigma w(|F_{obs}|-|F_{cal}|)^2)/\Sigma w F_{obs}^2)^{0.5}$, was 9.3%.

The reflections whose integrated intensities were judged to be unobservable (i.e. either negative or values less than σ_{cs}) had previously been excluded from the refinement. These intensities, numbering nearly 300, constituted nearly one-seventh of the data set so it was decided to include them in the data. First, however, they were assigned minimum observable values. The minimum

TABLE   8

Shifts of Counter Metal
Positions From Film Data Positions

	Sb(1)	Sb(2)	Sb(3)	Sb(4)	
Δx*	.0016	-.0006	-.0016	.0002	
Δy	-.0020	-.0034	.0014	.0009	
Δz	-.0005	.0003	.0014	-.0002	

	Pb(1)	Pb(2)	Pb(3)	Pb(4)	Pb(5)
Δx	.00	.0027	-.0001	-.0005	-.0004
Δy	-.0039	.0013	.0019	.0010	-.0020
Δz	.00	-.0008	-.0008	.0000	-.0005

*(counter positions - film positions) = Δ

TABLE   9

Atomic Parameters

Sb(1) x = 0.5067 ± .0002
         y = 0.3328 ± .0005
         z = 0.4740 ± .0001
         β_{11} = 0.0017 ± .00019
         β_{22} = 0.00030 ± .00088
         β_{33} = 0.00063 ± .00006
         β_{12} = 0.00018 ± .00026
         β_{13} = 0.00033 ± .00008
         β_{23} = -0.00001 ± .00016

Sb(2) x = 0.4841 ± .0002
         y = 0.9420 ± .0005
         z = 0.4252 ± .0001
         β_{11} = 0.00143 ± .00018
         β_{22} = 0.00028 ± .00090
         β_{33} = 0.00069 ± .00006
         β_{12} = -0.00010 ± .00027
         β_{13} = 0.00038 ± .00007
         β_{23} = 0.00003 ± .00016

Sb(3) x = 0.2232 ± .0002
         y = 0.3230 ± .0005
         z = 0.3793 ± .0001
         β_{11} = 0.00176 ± .00018
         β_{22} = 0.00021 ± .00087
         β_{33} = 0.00052 ± .00005
         β_{12} = 0.00022 ± .00026
         β_{13} = 0.00037 ± .00007
         β_{23} = 0.00029 ± .00015

Sb(4) x = 0.4522 ± .0002
         y = 0.2586 ± .0005
         z = 0.3160 ± .0001
         β_{11} = 0.00170 ± .00018
         β_{22} = 0.00163 ± .00090
         β_{33} = 0.00057 ± .000054
         β_{12} = 0.00011 ± .00027
         β_{13} = 0.00041 ± .00007
         β_{23} = -0.00018 ± .00015

TABLE 9
(continued)

Atomic Parameters

Pb(1) x $=$ 0.5000 $\pm$ .00
          y $=$ 0.9557 $\pm$ .0004
          z $=$ 0.2500 $\pm$ .00
          β_{11} $=$ 0.00292 $\pm$ .00018
          β_{22} $=$ 0.00121 $\pm$ .00082
          β_{33} $=$ 0.00081 $\pm$ .00005
          β_{12} $=$ 0.0
          β_{13} $=$ 0.00020 $\pm$ .00080
          β_{23} $=$ 0.0

Pb(2) x $=$ 0.2276 $\pm$ .0001
          y $=$ 0.0143 $\pm$ .0003
          z $=$ 0.3068 $\pm$ .0001
          β_{11} $=$ 0.00185 $\pm$ .00011
          β_{22} $=$ 0.00110 $\pm$ .00052
          β_{33} $=$ 0.00060 $\pm$ .00003
          β_{12} $=$ 0.00027 $\pm$ .00016
          β_{13} $=$ 0.00020 $\pm$ .00004
          β_{23} $=$ $-$ .00007 $\pm$ .00009

Pb(3) x $=$ 0.2683 $\pm$ .0001
          y $=$ 0.2275 $\pm$ .0003
          z $=$ 0.0927 $\pm$ .0001
          β_{11} $=$ 0.00184 $\pm$ .00011
          β_{22} $=$ 0.00106 $\pm$ .00054
          β_{33} $=$ 0.00064 $\pm$ .00003
          β_{12} $=$ -0.00015 $\pm$ .00017
          β_{13} $=$ 0.00033 $\pm$ .00004
          β_{23} $=$ 0.00000 $\pm$ .00009

Pb(4) x $=$ 0.0226 $\pm$ .0001
          y $=$ 0.1151 $\pm$ .0003
          z $=$ 0.1426 $\pm$ .0001
          β_{11} $=$ 0.00189 $\pm$ .00011
          β_{22} $=$ 0.00005 $\pm$ .00050
          β_{33} $=$ 0.00074 $\pm$ .00003
          β_{12} $=$ 0.00010 $\pm$ .00016
          β_{13} $=$ 0.00038 $\pm$ .00004
          β_{23} $=$ 0.00014 $\pm$ .00009

TABLE   9
(continued)

Atomic Parameters

Pb(5)   x = 0.2498 ± .0002
          y = 0.0527 ± .0003
          z = 0.4821 ± .0001
          β_{11} = 0.00252 ± .00012
          β_{22} = 0.00227 ± .00054
          β_{33} = 0.00070 ± .00003
          β_{12} = 0.00022 ± .00018
          β_{13} = 0.00036 ± .00005
          β_{23} = -0.00006 ± .00010

S (1)   x = 0.0   ± 0.0
          y = 0.8955 ± .0024
          z = 0.25   ± 0.0
          β = 1.4877 ± .3531

S (2)   x = 0.3212 ± .0009
          y = 0.4036 ± .0018
          z = 0.3174 ± .0005
          β = 1.2424 ± .2335

S (3)   x = 0.1106 ± .0008
          y = 0.4969 ± .0019
          z = 0.3698 ± .0005
          β = 0.9574 ± .2168

S (4)   x = 0.3675 ± .0009
          y = 0.1145 ± .0018
          z = 0.4013 ± .0005
          β = 1.1160 ± .2346

S (5)   x = 0.3810 ± .0009
          y = 0.5515 ± .0018
          z = 0.4524 ± .0005
          β = 1.1254 ± .2200

S (6)   x = 0.3714 ± .0009
          y = 0.4421 ± .0019
          z = 0.1020 ± .0005
          β = 1.3432 ± .2317

S (7)   x = 0.1235 ± .0009
          y = 0.3383 ± .0019
          z = 0.1524 ± .0005
          β = 1.2759 ± .2346

TABLE   9
(continued)

Atomic Parameters

S (8)   x =   0.1112 ±   .0008
           y =   0.2221 ±   .0019
           z =   0.3033 ±   .0005
           β =   1.1645 ±   .2268

S (9)   x =   0.3571 ±   .0010
           y =   0.1335 ±   .0019
           z =   0.2440 ±   .0005
           β =   1.5033 ±   .2345

S(10)   x =   0.0958 ±   .0009
           y =   0.2190 ±   .0019
           z =   0.4557 ±   .0005
           β =   1.3511 ±   .2345

S(11)   x =   0.3662 ±   .0009
           y =   0.1734 ±   .0018
           z =   0.0017 ±   .0005
           β =   1.1604 ±   .2232

recordable intensity (I_{min}) that is statistically meaningful may
be defined as

$$I_{min} = E_{min} - B,$$

where E_{min} is the smallest meaningful peak expressed as

$$E_{min} = PE(E) + B + PE(B),$$

where PE(E) is the probable error in E (i.e. 0.6745 σ_E) and PE(B)
is the probable error in the background B (i.e. 0.6745 σ_B).
Finally the intensity of a statistically unobservable peak is for
a centric structure

$$I_{unobs} = (1/3)\ I_{min}.$$

Thus this procedure was followed for approximately 300 reflections.
They were added to the data set but excluded from the refinement
process.

In the last cycles of refinement the metal atoms and finally
the sulfurs were allowed to vibrate anisotropically. This was
meaningful for the metal atoms, but for the sulfur atoms such
motion produced negative temperature factors so they were con-
strained to isotropic motion. Temperature factors, the scale
factor and the atomic positions were all refined until convergence.
The final discrepancy index was R(including unobs.)=11.3% ,
R(omitting unobs.)=10.0%, and R_W = 8.3%. The final atomic para-
meters are given in Table 9. Ellipsoids of thermal vibration are
given in Table 10 for the metal atoms. The structure factors are
reported in Table 11.

As a side note, this data set was used as input to FAME. A

TABLE   10

Principal Axes and Orientations
Of Thermal-Vibration Ellipsoids

Atom	Principal Axes	RMS Amplitude	Orientation With Respect To		
			a	b	c
Sb(1)	1	0.044 (70) Å	97°(10)	7°(11)	87°(9)
	2	0.120 (8)	9°(18)	83°(11)	112°(24)
	3	0.133 (6)	94°(24)	90°(9)	22°(24)
Sb(2)	1	0.043 (74)	96°(14)	174°(15)	87°(9)
	2	0.107 (8)	7°(13)	96°(15)	110°(9)
	3	0.140 (6)	86°(9)	89°(7)	20°(9)
Sb(3)	1	0.020 (150)	89°(10)	164°(9)	75°(11)
	2	0.113 (9)	34°(17)	98°(10)	138°(18)
	3	0.131 (5)	56°(17)	77°(8)	52°(16)
Sb(4)	1	0.096 (24)	120°(29)	42°(35)	56°(23)
	2	0.120 (14)	37°(26)	54°(28)	109°(42)
	3	0.132 (7)	70°(27)	108°(30)	40°(15)
Pb(1)	1	0.093 (32)	90°	0°	90°
	2	0.145 (31)	117°(32)	90°	136°(32)
	3	0.171 (48)	153°(32)	90°	47°(32)
Pb(2)	1	0.085 (21)	104°(9)	14°(8)	83°(7)
	2	0.124 (3)	130°(12)	97°(8)	124°(12)
	3	0.138 (5)	137°(10)	103°(8)	35°(12)
Pb(3)	1	0.086 (22)	81°(10)	8°(10)	93°(8)
	2	0.126 (5)	9°(13)	98°(10)	110°(21)
	3	0.134 (3)	86°(21)	90°(8)	20°(21)
Pb(4)	1	0.014 (130)	89°(5)	174°(4)	85°(4)
	2	0.126 (4)	3°(8)	89°(5)	109°(9)
	3	0.145 (3)	87°(9)	84°(4)	20°(8)
Pb(5)	1	0.124 (14)	108°(13)	22°(18)	73°(20)
	2	0.140 (4)	94°(21)	78°(17)	157°(23)
	3	0.150 (5)	18°(15)	72°(15)	105°(18)

TABLE 11
Comparison of F_{obs} with F_{cal}

h	k	F_{obs}	F_{cal}

This page contains an extensive crystallographic structure-factor listing arranged in multiple vertical columns. Each column group is headed by an index value (e.g. $k = 0$, $k = 1$, $k = 2$, $k = 3$) and the repeated sub-headings h, k (ℓ), F_{obs}, F_{cal}. The tabulated reflection data consist of thousands of numeric entries that are too densely printed to transcribe reliably.

Table 11 (cont.)   50

Structure factor listing (columns: h, k, l, F_{obs}, F_{cal}). Section labels present include "h l F_{obs} F_{cal}", "k = 4", and "k = 5".

Wilson calculation was made yielding an overall scale factor of 0.5100 and an overall temperature factor of 1.3825. This compares with the final scale factor from the refinement process of 0.4772. The statistics indicate a centric structure and are given in Table 12.

TABLE 12

Statistical Distribution of E's Calculated
From Wilson Plot

(Counter Data)

Quantity	Calculated	Theoretical (Centric)	Theoretical (Acentric)
Average Mag of E's	0.810	0.798	0.886
Average of E^2	0.994	1.000	.1000
Average of $\lvert E^2 - 1 \rvert$	0.976	0.968	0.736
Percentage Greater Than One	28.68	32.00	37.00
Percentage Greater Than Two	5.47	5.00	1.80
Percentage Greater Than Three	0.33	0.30	0.01

Chapter VI

Description of the Structure

Semseyite is a complicated structure which may be best understood by viewing it in two different projections. The first is the standard (010) projection. The second is a projection onto (112). Before discussing the total structure, the individual polyhedra will be examined. There are twenty atoms in the asymmetric unit: five Pb, four Sb, and eleven S. All the antimony atoms occupy the general position as do four of the lead atoms and ten of the sulfur. The remaining lead and sulfur atoms occupy equipoint (4e) at (0,y,0.25).

A.   The Polyhedra

The lead coordination polyhedra are basically of three types: an eight-coordinate Pb, a seven coordinate and three of either five or six coordination. The eight-fold coordinated lead atom, Pb(1), is the one that occupies the special position with two-fold symmetry. It can be described as a square-antiprism with top and bottom of the antiprism related by the two-fold axis. The lead atom has four close sulfur neighbors, $S(9^1)$, $S(9^3)$ at 2.85A° and $S(3^5)$, $S(3^7)$ at 2.94 A°. A third pair of sulfur atoms, $S(8^5)$ and $S(8^7)$, occur at a distance of 3.27 A°; while the fourth pair, $S(7^5)$ and $S(7^7)$, is at a distant 3.56 A°.

The remaining lead coordination polyhedra are characterized by a "split-vertex" which is simply the vertex below the equatorial plane being occupied by two atoms - splitting the vertex into two parts. Pb(2), the seven-coordinated lead atom, occupies the

general position. The general form of the polyhedron is an octahedron with a 'split' sixth vertex. $S(4^1)$ occupies an apex at a distance of 2.82 A° above an equatorial plane comprised of four sulfur atoms, $S(7^7)$, $S(8^1)$, $S(9^1)$, and $S(6^7)$ at distances of 2.90, 2.93, 3.00, and 3.03 A° respectively. The 'split' vertex is composed of $S(2^7)$ and $S(1^1)$ at distances of 3.21 and 3.34 A°.

Of the three remaining lead atoms two, Pb(3) and Pb(4), are quite simply described as six-coordinated by sulfur. The third lead, Pb(5), is predominately five-coordinated with a longer distance to a sixth sulfur. All of these polyhedra are octahedra with the vertex below the equatorial plane displaced. Pb(3) has an apical sulfur, $S(11^6)$ at 2.78A° and four sulfur atoms in the equatorial plane, $S(6^1)$, $S(5^7)$, $S(11^1)$ and $S(7^1)$ at distances of 2.90, 2.92, 2.96, and 3.06 A° respectively. The displaced vertex sulfur is $S(3^7)$ at 3.21 A°. Pb(4) has similar octahedral coordination with one vertex displaced. The apical sulfur, $S(10^2)$, is located at 2.79 A° while the equatorial sulfurs, $S(8^3)$, $S(6^5)$, $S(7^1)$, and $S(5^7)$ are at distances of 2.83, 2.89, 2.98 and 3.06 A° respectively. The sixth, displaced, vertex sulfur, $S(2^7)$, is located at 3.27 A°. The final lead Pb(5) is really best described as five-coordinated; the sixth sulfur is at a much larger distance. The apex of the 'octahedron' is $S(6^7)$ at a distance of 2.61 A° from Pb(5). The equatorial plane contains sulfurs, $S(10^1)$, $S(4^1)$, $S(5^6)$ and $S(11^4)$ at 2.83, 2.96, 2.98, and 3.10 A° respectively. The almost missing displaced vertex sulfur, $S(10^6)$ occurs at 3.52 A°

completing the six sulfur coordination scheme.

With each of these three Pb-polyhedra it is possible to lo-
cate a seventh sulfur neighbor which would change the 'displaced-
vertex' scheme to a 'split-vertex' octahedron. This polyhedral
description would then resemble the coordination of Pb(2). For
Pb(3) the seventh neighbor, S(9^1), occurs at 3.73 A°, for Pb(4),
S(1^1) comes at 3.78 A° and for Pb(5), S(3^6) comes at 3.64 A°. Thus
all the lead atoms occupying the general position have very similar
polyhedral configuration, seven-coordinate; although the seventh
neighbors occur at distances ranging from 3.34 A° to 3.78A° . Con-
sidering the sulfurs in the equatorial plane of these three Pb-
polyhedron, the average Pb-S bond distance for the four Pb-S bonds
in the plane is 2.96, 2.93, and 2.96 A° for Pb(3), Pb(4), and Pb(5)
polyhedra respectively. The equatorial average for the seven-co-
ordinate Pb(2) is 3.04 A°. Thus these four polyhedra can be seen
to resemble closely each other. The bond distances, bond angles,
and errors for the five Pb-polyhedra are given in Table 13. The
polyhedra themselves are presented in Figure 3.

The four antimony atoms in the asymmetric unit all occupy the
general position. They are basically of two types: five-coordinated
by sulfur and three-coordinated. Sb(1), Sb(2), Sb(3) have the
first coordination while Sb(4) has the latter scheme. Sb(1) has
a square pyramid of sulfurs surrounding it. The apical sulfur,
S(5^2) occurs at a distance of 2.44 A°. The basal plane has four
sulfurs, S(11^3), S(10^6), S(5^1), and S(6^3), at distances of 2.53,
2.57, 3.08, and 3.10 A° respectively. Sb(2) has a similar square

Figure 3

Pb-Coordination Polyhedron - Semseyite
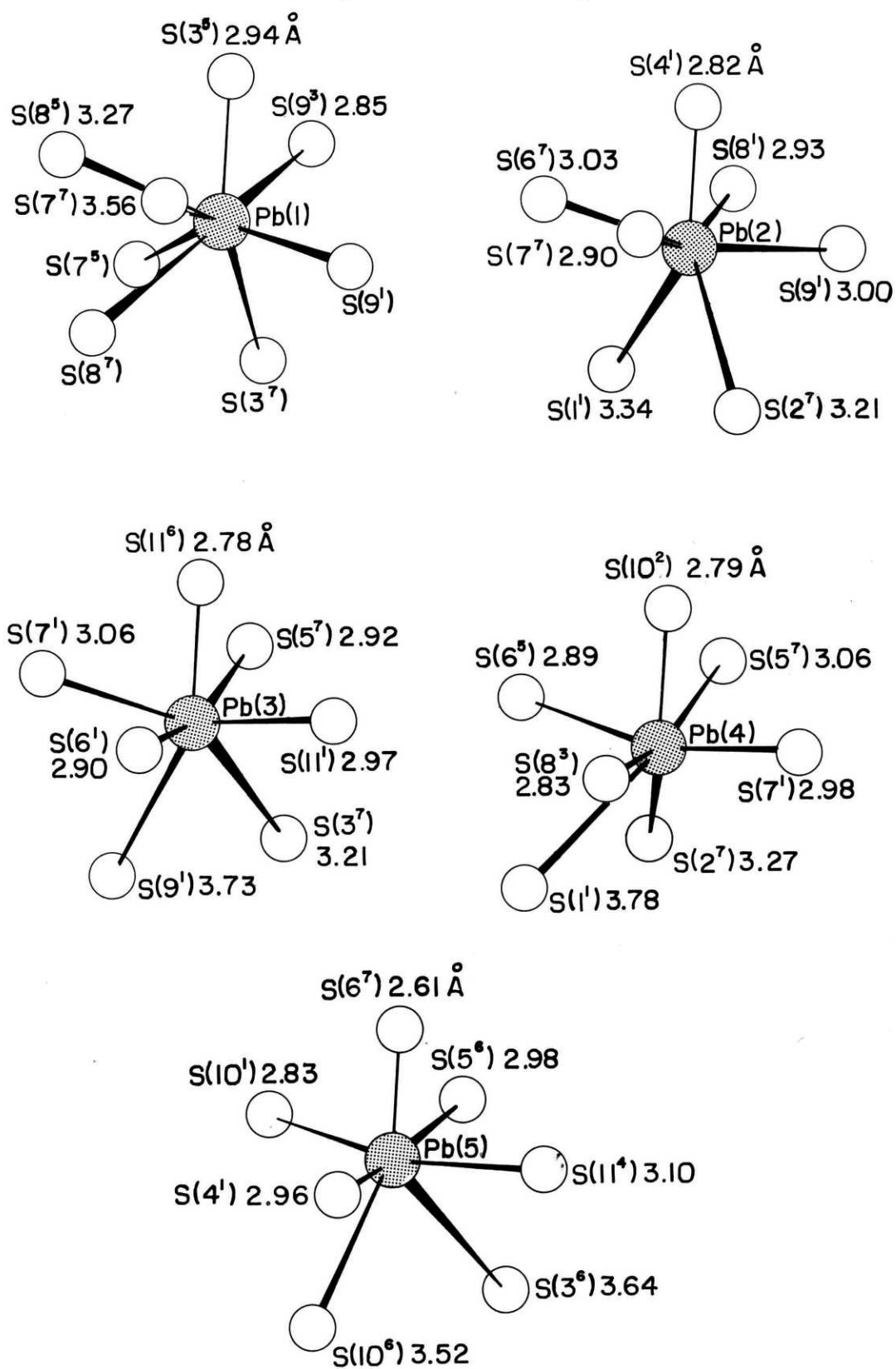
TABLE   13

Pb-S Bond Distances and Angles

A. Bond Distances

Pb(1)

S(9^1)	2.854	(20) Å
S(9^3)	2.854	(20)
S(3^5)	2.942	(11)
S(3^7)	2.942	(11)
S(8^5)	3.267	(20)
S(8^7)	3.267	(20)
S(7^5)	3.564	(16)
S(7^7)	3.564	(16)

Pb(2)

S(4^1)	2.820	(13) Å
S(7^7)	2.897	(18)
S(8^1)	2.931	(20)
S(6^7)	3.031	(15)
S(9^1)	2.998	(17)
S(2^7)	3.211	(14)
S(1^1)	3.339	(12)

Pb(3)

S(11^6)	2.782	(13) Å
S(6^1)	2.899	(21)
S(5^7)	2.918	(17)
S(11^1)	2.965	(14)
S(7^1)	3.057	(16)
S(3^7)	3.208	(20)
S(9^1)	3.731	(14)

Pb(4)

S(10^2)	2.789	(14) Å
S(8^3)	2.833	(16)
S(6^5)	2.890	(18)
S(7^1)	2.976	(21)
S(5^7)	3.061	(14)
S(2^7)	3.270	(19)
S(1^1)	3.782	(20)

Pb(5)

S(6^7)	2.610	(15) Å
S(10^1)	2.829	(18)
S(4^1)	2.959	(14)
S(5^6)	2.978	(15)
S(11^4)	3.098	(20)
S(10^6)	3.518	(19)
S(3^6)	3.642	(11)

TABLE   13
(continued)

Pb-S Bond Distances and Angles

B. Bond Angles

Pb(1)

S(9^1)	- Pb -	S(9^3)	83.93(75)		degrees
S(9^1)	- Pb -	S(3^7)	70.75(44)	2x	
S(9^1)	- Pb -	S(3^5)	94.65(46)	2x	
S(9^1)	- Pb -	S(7^7)	83.49(46)	2x	
S(9^1)	- Pb -	S(7^5)	134.27(39)	2x	
S(9^1)	- Pb -	S(8^5)	152.75(40)	2x	
S(9^1)	- Pb -	S(8^7)	112.34(42)	2x	
S(3^5)	- Pb -	S(3^7)	160.75(89)		
S(3^5)	- Pb -	S(7^7)	66.72(37)	2x	
S(3^5)	- Pb -	S(7^5)	121.78(33)	2x	
S(3^5)	- Pb -	S(8^7)	126.38(50)	2x	
S(3^5)	- Pb -	S(8^5)	72.07(49)	2x	
S(7^5)	- Pb -	S(7^7)	133.70(71)		
S(7^5)	- Pb -	S(8^7)	69.47(39)	2x	
S(7^5)	- Pb -	S(8^5)	71.31(39)	2x	
S(8^5)	- Pb -	S(8^7)	62.82(51)		

Pb(2)

S(4^1)	- Pb -	S(6^7)	81.65(41)	degrees
S(4^1)	- Pb -	S(7^7)	77.08(51)	
S(4^1)	- Pb -	S(8^1)	84.38(46)	
S(4^1)	- Pb -	S(9^1)	81.93(41)	
S(4^1)	- Pb -	S(1^1)	149.22(29)	
S(4^1)	- Pb -	S(2^7)	149.95(37)	
S(6^7)	- Pb -	S(7^7)	87.21(45)	
S(6^7)	- Pb -	S(8^1)	85.18(49)	
S(7^7)	- Pb -	S(9^1)	93.82(47)	
S(9^1)	- Pb -	S(8^1)	88.42(51)	
S(7^7)	- Pb -	S(8^1)	160.80(38)	
S(6^7)	- Pb -	S(9^1)	162.88(47)	
S(1^1)	- Pb -	S(2^7)	60.40(27)	
S(1^1)	- Pb -	S(6^7)	68.67(25)	
S(1^1)	- Pb -	S(7^7)	108.37(57)	
S(1^1)	- Pb -	S(8^1)	85.17(52)	
S(1^1)	- Pb -	S(9^1)	126.61(27)	
S(2^7)	- Pb -	S(6^7)	124.19(46)	
S(2^7)	- Pb -	S(7^7)	88.24(43)	
S(2^7)	- Pb -	S(8^1)	110.59(39)	
S(2^7)	- Pb -	S(9^1)	72.93(44)	

TABLE   13
(continued)

Pb-S Bond Distances and Angles

B. Bond Angles

Pb(3)

$S(11^6)$ - Pb - $S(7^1)$	81.33(40)	degrees
$S(11^6)$ - Pb - $S(6^1)$	83.23(48)	
$S(11^6)$ - Pb - $S(11^1)$	78.37(47)	
$S(11^6)$ - Pb - $S(5^7)$	76.30(50)	
$S(11^6)$ - Pb - $S(9^1)$	155.31(38)	
$S(11^6)$ - Pb - $S(3^7)$	140.31(47)	
$S(5^7)$ - Pb - $S(11^1)$	88.27(44)	
$S(5^7)$ - Pb - $S(7^1)$	91.08(45)	
$S(7^1)$ - Pb - $S(6^1)$	86.68(50)	
$S(6^1)$ - Pb - $S(11^1)$	86.72(50)	
$S(5^7)$ - Pb - $S(6^1)$	159.51(40)	
$S(11^1)$ - Pb - $S(7^1)$	159.25(43)	
$S(9^1)$ - Pb - $S(3^7)$	57.26(39)	
$S(9^1)$ - Pb - $S(7^1)$	74.45(37)	
$S(9^1)$ - Pb - $S(6^1)$	99.87(40)	
$S(9^1)$ - Pb - $S(11^1)$	126.11(39)	
$S(9^1)$ - Pb - $S(5^7)$	99.13(41)	
$S(3^7)$ - Pb - $S(7^1)$	125.63(43)	
$S(3^7)$ - Pb - $S(6^1)$	122.47(40)	
$S(3^7)$ - Pb - $S(11^1)$	74.09(44)	
$S(3^7)$ - Pb - $S(5^7)$	74.86(43)	

Pb(4)

$S(10^2)$ - Pb - $S(6^5)$	80.47(51)	degrees
$S(10^2)$ - Pb - $S(5^7)$	73.90(42)	
$S(10^2)$ - Pb - $S(8^3)$	84.78(42)	
$S(10^2)$ - Pb - $S(7^1)$	79.31(47)	
$S(10^2)$ - Pb - $S(2^7)$	140.69(45)	
$S(10^2)$ - Pb - $S(1^1)$	140.21(35)	
$S(7^1)$ - Pb - $S(5^7)$	89.90(47)	
$S(7^1)$ - Pb - $S(8^3)$	84.31(51)	
$S(8^3)$ - Pb - $S(6^5)$	89.66(48)	
$S(6^5)$ - Pb - $S(5^7)$	88.58(44)	
$S(2^7)$ - Pb - $S(1^1)$	55.17(33)	
$S(2^7)$ - Pb - $S(6^5)$	83.88(47)	
$S(2^7)$ - Pb - $S(5^7)$	69.87(40)	
$S(2^7)$ - Pb - $S(8^3)$	131.09(41)	
$S(2^7)$ - Pb - $S(7^1)$	114.83(40)	
$S(1^1)$ - Pb - $S(6^5)$	63.71(35)	
$S(1^1)$ - Pb - $S(5^7)$	119.27(49)	
$S(1^1)$ - Pb - $S(8^3)$	78.59(47)	
$S(1^1)$ - Pb - $S(7^1)$	133.55(34)	

TABLE   13
(continued)

Pb-S Bond Distances and Angles

B. Bond Angles

Pb(5)

S(6^7) - Pb - S(10^1)	84.74(52)	degrees
S(6^7) - Pb - S(4^1)	86.62(43)	
S(6^7) - Pb - S(11^4)	82.29(50)	
S(6^7) - Pb - S(5^6)	82.59(43)	
S(6^7) - Pb - S(10^6)	154.66(49)	
S(6^7) - Pb - S(3^6)	137.98(56)	
S(10^1) - Pb - S(4^1)	100.15(47)	
S(4^1) - Pb - S(11^4)	88.45(47)	
S(11^4) - Pb - S(5^6)	84.77(46)	
S(5^6) - Pb - S(10^1)	84.27(48)	
S(10^6) - Pb - S(3^6)	67.12(42)	
S(3^6) - Pb - S(10^1)	119.34(40)	
S(3^6) - Pb - S(4^1)	118.37(29)	
S(3^6) - Pb - S(11^4)	66.51(40)	
S(3^6) - Pb - S(5^6)	67.75(30)	
S(10^6) - Pb - S(10^1)	82.58(33)	
S(10^6) - Pb - S(4^1)	74.20(41)	
S(10^6) - Pb - S(11^4)	112.93(38)	
S(10^6) - Pb - S(5^6)	117.68(39)	
S(4^1) - Pb - S(5^6)	167.93(52)	
S(10^1) - Pb - S(11^4)	163.98(47)	

pyramidal coordination. $S(7^7)$ is the apical sulfur at a distance of 2.40 A° while the basal plane is composed of $S(3^5)$, $S(4^1)$, $S(10^5)$, and $S(11^4)$ at distances of 2.55, 2.57, 3.05, 3.10 A° respectively. Sb(3) again has the square-pyramidal coordination by sulfur. The apex sulfur, $S(8^1)$ is located 2.38 A° from the antimony atom. The basal plane sulfur atoms are $S(2^1)$, $S(3^1)$, $S(4^1)$, and $S(10^1)$, at distances of 2.47, 2.55, 3.12, and 3.13 A° respectively. The final antimony atom, Sb(4), is primarily three-coordinated. The shortest distance in the trigonal pyramid (considering the antimony atom as a vertex) is $S(9^1)$ which is at 2.40 A°. The other vertices $S(2^1)$ and $S(1^3)$ occur at 2.49 and 2.51 A° respectively shorter than second and third neighbors in the other polyhedra. It should be noticed that fourth and fifth neighbors can be found for Sb(4) but at much larger distances, $S(4^1)$ at 3.16 and $S(9^3)$ at 3.63 A°. This generates a polyhedron similar to those of Sb(1), Sb(2), and Sb(3).

Interestingly, an additional neighbor for each antimony can be found resulting in a polyhedron resembling that of the 'split-vertex' octahedron for Pb. To do this requires consideration of sulfurs at non-bonding distances. For Sb(1), $S(4^1)$ at 3.42 A° and $S(2^2)$ at 4.05 A° complete the 'split-vertex' octahedron, for Sb(2) $S(11^3)$ at 3.60 A° and $S(4^2)$ at 4.22 A°, for Sb(3) $S(5^1)$ at 3.62 A° and $S(10^6)$ at 4.13 A°, and for Sb(4) in addition to the two sulfurs already added $S(6^3)$ at 3.45 A° and $S(3^5)$ at 3.82 A° complete the coordination. The bond distances, bond angles, and errors are presented in Table 14. The Sb polyhedra are shown in Figure 4.

FIGURE 4

Sb Coordination Polyhedra - Semseyite

S(5^2) 2.44 Å
S(5^1) 3.08
S(10^6) 2.57
S(6^3) 3.10
Sb(1)
S(11^3) 2.53
S(2^1) 4.05
S(4^1) 3.41

S(7^7) 2.40 Å
S(11^4) 3.10
S(4^1) 2.56
S(10^5) 3.05
Sb(2)
S(3^5) 2.57
S(4^2) 4.23
S(11^3) 3.60

S(8^1) 2.38 Å
S(10^1) 3.13
S(3^1) 2.55
S(4^1) 3.12
Sb(3)
S(2^1) 2.47
S(10^6) 4.14
S(5^1) 3.62

S(9^1) 2.40 Å
S(4^1) 3.16
S(9^3) 3.63
S(2^1) 2.49
Sb(4)
S(1^3) 2.51
S(3^5) 3.82
S(6^3) 3.45
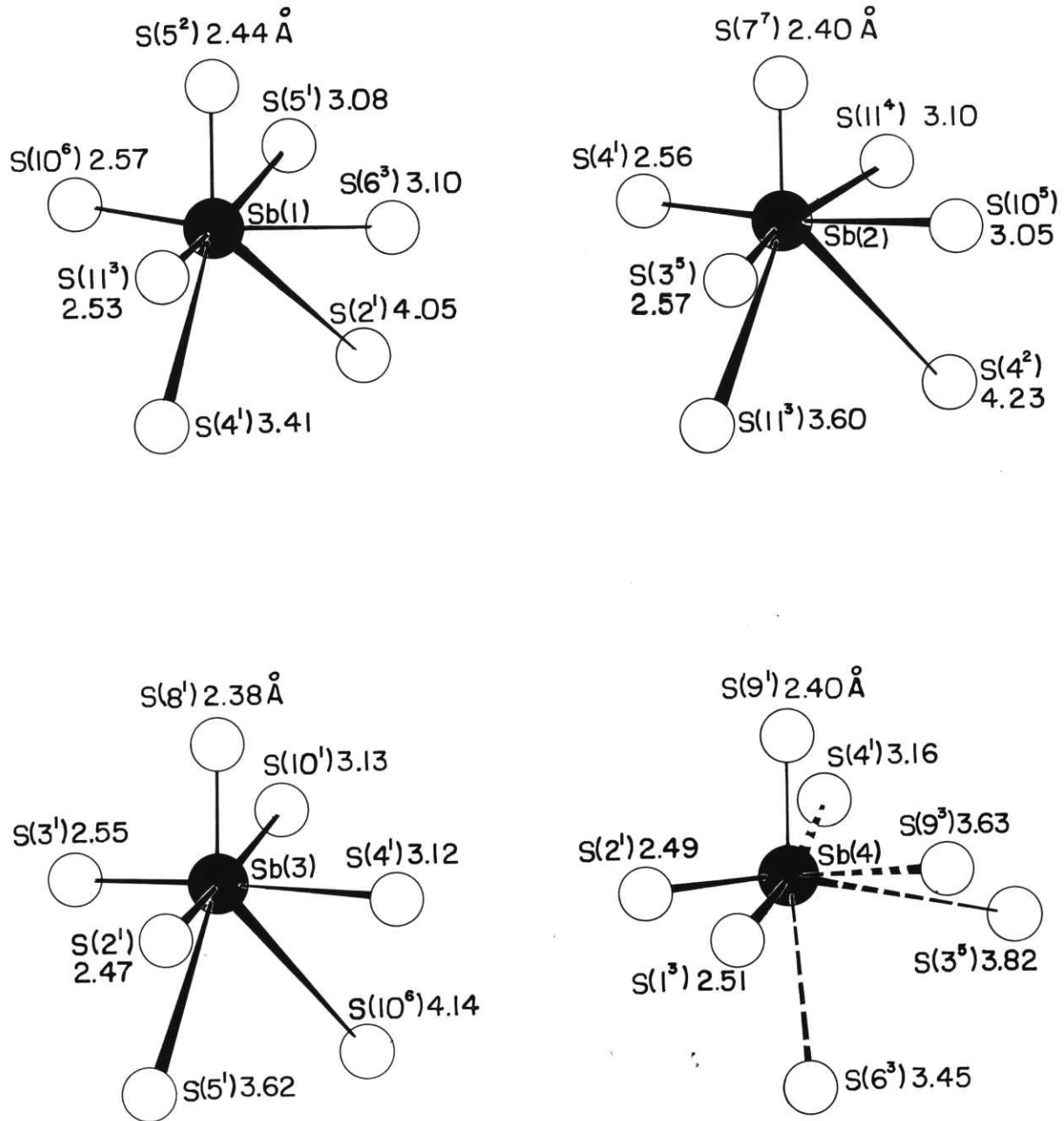
TABLE 14

Sb-S Bond Distances and Angles

A. Bond Distances

Sb(1)   Sb(2)

S(5^2)	2.441(15)	Å
S(11^3)	2.528(19)	
S(10^6)	2.570(15)	
S(5^1)	3.085(20)	
S(6^3)	3.100(16)	
[S(4^1)	3.418(18)]	
[S(2^1)	4.050(12)]	

S(7^7)	2.395(15)	Å
S(3^5)	2.553(14)	
S(4^1)	2.566(19)	
S(10^5)	3.053(21)	
S(11^4)	3.102(16)	
[S(11^3)	3.601(19)]	
[S(4^2)	4.219(12)]	

Sb(3)   Sb(4)

S(8^1)	2.378(14)	Å
S(2^1)	2.470(16)	
S(3^1)	2.552(20)	
S(4^1)	3.123(20)	
S(10^1)	3.134(16)	
[S(5^1)	3.622(18)]	
[S(10^6)	4.136(12)]	

S(9^1)	2.398(17)	Å
S(2^1)	2.492(18)	
S(1^3)	2.506(19)	
[S(4^1)	3.157(17)]	
[S(6^3)	3.453(17)]	
[S(9^3)	3.635(19)]	
[S(3^5)	3.817(20)]	

B. Bond Angles

Sb(1)

S(5^2) – Sb – S(10^6)	89.30(49)	degrees
S(5^2) – Sb – S(11^3)	90.27(54)	
S(5^2) – Sb – S(5^1)	81.50(41)	
S(5^2) – Sb – S(6^3)	82.81(46)	
S(10^6) – Sb – S(11^3)	97.10(56)	
S(11^3) – Sb – S(6^3)	90.77(50)	
S(6^3) – Sb – S(5^1)	84.49(47)	
S(11^3) – Sb – S(5^1)	170.94(49)	
S(10^6) – Sb – S(6^3)	168.89(66)	
S(5^1) – Sb – S(10^6)	86.63(54)	

TABLE   14
(continued)

Sb-S Bond Distances and Angles

B. Bond Angles

Sb(2)

S(7^7) - Sb - S(4^1)   91.74(56)   degrees
S(7^7) - Sb - S(3^5)   93.81(48)
S(7^7) - Sb - S(11^4)   86.77(48)
S(7^7) - Sb - S(10^5)   84.09(56)
S(4^1) - Sb - S(3^5)   97.93(58)
S(3^5) - Sb - S(10^5)   89.43(55)
S(10^5) - Sb - S(11^4)   76.77(46)
S(11^4) - Sb - S(4^1)   116.82(28)
S(11^4) - Sb - S(3^5)   166.06(57)
S(4^1) - Sb - S(10^5)   171.79(48)

Sb(3)

S(8^1) - Sb - S(3^1)   95.87(54)   degrees
S(8^1) - Sb - S(2^1)   93.25(49)
S(8^1) - Sb - S(10^1)   85.70(46)
S(8^1) - Sb - S(4^1)   88.14(54)
S(2^1) - Sb - S(4^1)   89.79(53)
S(4^1) - Sb - S(10^1)   90.40(47)
S(10^1) - Sb - S(3^1)   87.65(51)
S(3^1) - Sb - S(2^1)   92.24(59)
S(2^1) - Sb - S(10^1) 178.92(38)
S(4^1) - Sb - S(3^1)   175.39(36)

Sb(4)

S(9^1) - Sb - S(2^1)   101.55(53)   degrees
S(9^1) - Sb - S(1^3)   96.70(56)
S(9^1) - Sb - S(9^3)   75.42(55)
S(9^1) - Sb - S(4^1)   85.67(51)
S(2^1) - Sb - S(1^3)   82.54(58)
S(1^3) - Sb - S(9^3)   70.56(55)
S(9^3) - Sb - S(4^1)   118.29(50)
S(4^1) - Sb - S(2^1)   88.61(51)
S(1^3) - Sb - S(4^1)   171.13(57)
S(2^1) - Sb - S(9^3)   152.18(48)

There are eleven sulfur atoms in the asymmetric unit - ten in the general position and one in the special position 4e, S(1). Basically there are two types of sulfur coordination polyhedra - four coordinate and either five or six coordinate. Five of the sulfur atoms fall in the first category and six in the latter.

The four-coordinated sulfur atoms all have distorted tetrahedra of metals. These sulfurs are S(1), S(2), S(3), S(8), and S(9). The remaining sulfur atoms are all six-coordinated with the exception of S(7) which is five-coordinated. In some cases the sixth neighbor is at large distances. The six-coordinated sulfur atoms are S(4), S(5), S(6), S(10), and S(11). All the sulfur coordination polyhedra are shown in Figure 5. Bond distances and angles and the associated errors are given in Table 15. The sulfur-sulfur contact distances in the metal polyhedra are reported in Table 16.

B. Projections of the Structure

Semseyite may be understood by studying it in two projections, (010) and (112). These projections are presented as Figures 6 and 7 respectively.

The (010) projection (Figure 6) looks like a complete jumble on first glance. However, study reveals that the lead atom on the two-fold special position, Pb(1), acts as a pivot point for what appears to be chains of lead and antimony atoms. These 'chains' run parallel to the c axis and occur at x = 0,.25,.5,and .75. Basically there are two types of 'chains'. Those occuring at x = 0, 0.5 are antimony 'chains' with a few lead atoms. They contain

Figure 5   66

S – Coordination Polyhedra – Semseyite

Sb(4⁷) 2.51 Å
Pb(2')3.34   S(1)
Pb(2³)   Sb(4⁵)

Pb(4⁷) 3.27 Å
Sb(4') 2.49   S(2)
Pb(2⁷) 3.21   Sb(3')
               2.47

Sb(3') 2.55 Å
Sb(2⁵)   S(3)
2.55
Pb(1³) 2.94
Pb(3⁷) 3.21

Sb(3') 2.38 Å
Pb(1³)3.27   S(8)
Pb(4³)   Pb(2')2.93
2.83

Sb(4') 2.40 Å
              Sb(4³) 3.63
              S(9)
Pb(1') 2.85
              Pb(2') 3.00

Figure 5(cont.)

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Pb(2¹) 2.82 A
Sb(3¹) 3.12
Pb(5¹) 2.96
S(4)
Sb(4¹) 3.16
Sb(2¹) 2.57
Sb(1¹) 3.42

Sb(1²) 2.44 Å
Pb(3⁷) 2.82
Pb(4⁷) 3.06
S(5)
Pb(5⁶) 2.98
Sb(1¹) 3.08
Sb(3¹) 3.62

Pb(5⁷) 2.61 Å
Pb(4⁵) 2.89
Pb(2⁷) 3.03
S(6)
Sb(1⁵) 3.10
Pb(3¹) 2.90
Sb(4³) 3.45

Sb(2⁷) 2.40 Å
Pb(2⁷) 2.90
Pb(1³) 3.56
S(7)
Pb(3¹) 3.06
Pb(4¹) 2.98

Pb(3⁶) 2.78 Å
Sb(2³) 3.60
Pb(5⁴) 3.10
S(11)
Pb(3⁶) 2.78
Sb(1³) 2.53
Sb(2³) 3.60

Pb(4³) 2.79 Å
Sb(2⁵) 3.05
Sb(1⁶) 2.57
S(10)
Sb(3¹) 3.13
Pb(5¹) 2.83
Pb(5⁶) 3.52

TABLE   15

Sulfur-Metal Bond Distances and Angles

A. Bond Distances

S(1)			S(2)		
$Sb(4^7)$	2.506(19) Å		$Sb(3^1)$	2.470(16) Å	
$Sb(4^5)$	2.506(19)		$Sb(4^1)$	2.492(18)	
$Pb(2^3)$	3.339(12)		$Pb(2^7)$	3.211(14)	
$Pb(2^1)$	3.339(12)		$Pb(4^7)$	3.270(19)	

S(3)			S(4)		
$Sb(3^1)$	2.552(20) Å		$Sb(2^1)$	2.566(19) Å	
$Sb(2^5)$	2.553(14)		$Pb(2^1)$	2.820(13)	
$Pb(1^3)$	2.942(11)		$Pb(5^1)$	2.959(14)	
$Pb(3^7)$	3.208(20)		$Sb(3^1)$	3.123(19)	
			$Sb(4^1)$	3.157(17)	
			$Sb(1^1)$	3.418(18)	

S(5)			S(6)		
$Sb(1^2)$	2.441(15) Å		$Pb(5^7)$	2.610(15) Å	
$Pb(3^7)$	2.918(17)		$Pb(4^5)$	2.890(18)	
$Pb(5^6)$	2.978(15)		$Pb(3^1)$	2.899(21)	
$Pb(4^7)$	3.061(14)		$Pb(2^7)$	3.031(15)	
$Sb(1^1)$	3.085(20)		$Sb(1^3)$	3.100(16)	
$Sb(3^1)$	3.622(18)		$Sb(4^3)$	3.453(17)	

S(7)			S(8)		
$Sb(2^7)$	2.395(15) Å		$Sb(3^1)$	2.378(15) Å	
$Pb(2^7)$	2.897(18)		$Pb(4^3)$	2.833(16)	
$Pb(4^1)$	2.976(21)		$Pb(2^1)$	2.931(20)	
$Pb(3^1)$	3.057(16)		$Pb(1^3)$	3.267(20)	
$Pb(1^3)$	3.564(16)				

TABLE 15
(continued)

Sulfur-Metal Bond Distances and Angles

A. Bond Distances

S(9)

Sb(4^1)	2.398(17) Å
Pb(1^1)	2.854(20)
Pb(2^1)	2.998(17)
Sb(4^3)	3.635(17)

S(10)

Sb(1^6)	2.570(15) Å
Pb(4^3)	2.789(14)
Pb(5^1)	2.859(18)
Sb(2^5)	3.053(21)
Sb(3^1)	3.134(16)
Pb(5^6)	3.518(19)

S(11)

Sb(1^3)	2.528(19) Å
Pb(3^6)	2.782(13)
Pb(3^1)	2.965(14)
Pb(5^4)	3.098(20)
Sb(2^4)	3.102(16)
Sb(2^3)	3.601(19)

B. Bond Angles

S(1)

Sb(4^5) - S - Sb(4^7)	98.56(1.01)	degrees
Sb(4^7) - S - Pb(2^3)	112.62(16)	2x
Sb(4^7) - S - Pb(2^1)	99.74(12)	2x
Pb(2^3) - S - Pb(2^1)	129.77(89)	

S(2)

Pb(4^7) - S - Sb(4^1)	97.59(39)	degrees
Pb(4^7) - S - Pb(2^7)	84.96(47)	
Pb(4^7) - S - Sb(3^1)	122.29(53)	
Sb(4^1) - S - Pb(2^7)	103.50(45)	
Pb(2^7) - S - Sb(3^1)	137.27(43)	
Sb(3^1) - S - Sb(4^1)	104.31(75)	

TABLE 15
(continued)

Sulfur-Metal Bond Distances and Angles

B. Bond Angles

S(3)

Sb(3^1) - S - Pb(1^3)	94.77(56)	degrees
Sb(3^1) - S - Sb(2^5)	102.65(73)
Sb(3^1) - S - Pb(3^7)	115.10(39)
Pb(1^3) - S - Sb(2^5)	104.53(42)
Sb(2^5) - S - Pb(3^7)	115.92(59)
Pb(3^7) - S - Pb(1^3)	120.57(59)

S(4)

Pb(2^1) - S - Pb(5^1)	94.24(44)	degrees
Pb(2^1) - S - Sb(3^1)	86.97(33)
Pb(2^1) - S - Sb(4^1)	88.69(34)
Pb(2^1) - S - Sb(2^1)	94.65(64)
Pb(2^1) - S - Sb(1^1)	154.28(66)
Pb(5^1) - S - Sb(3^1)	83.30(38)
Sb(3^1) - S - Sb(4^1)	77.22(46)
Sb(2^1) - S - Sb(4^1)	105.82(46)
Sb(2^1) - S - Pb(5^1)	93.55(56)
Sb(4^1) - S - Pb(5^1)	160.13(73)
Sb(3^1) - S - Sb(2^1)	176.57(54)
Sb(1^1) - S - Sb(4^1)	71.18(40)
Sb(1^1) - S - Sb(3^1)	73.35(46)
Sb(1^1) - S - Pb(5^1)	99.58(41)
Sb(1^1) - S - Sb(2^1)	105.94(35)

S(5)

Sb(1^2) - S - Pb(3^7)	95.71(68)	degrees
Sb(1^2) - S - Pb(5^6)	100.63(42)
Sb(1^2) - S - Sb(1^1)	98.50(41)
Sb(1^2) - S - Pb(4^7)	96.17(52)
Sb(1^2) - S - Sb(3^1)	162.62(65)
Pb(3^7) - S - Pb(5^6)	92.68(38)
Pb(5^6) - S - Sb(1^1)	86.55(52)
Sb(1^1) - S - Pb(4^7)	90.40(41)
Pb(4^7) - S - Pb(3^7)	86.22(44)
Sb(3^1) - S - Pb(3^7)	95.75(29)
Sb(3^1) - S - Pb(5^6)	92.68(38)
Sb(3^1) - S - Sb(1^1)	95.75(29)
Sb(3^1) - S - Pb(4^7)	97.59(37)
Pb(4^7) - S - Pb(5^6)	163.20(56)
Pb(3^7) - S - Sb(1^1)	165.67(54)

TABLE 15
(continued)

Sulfur-Metal Bond Distances and Angles

B. Bond Angles

S(6)

$Pb(5^7)$ - S - $Pb(4^5)$	98.31(70)	degrees
$Pb(5^7)$ - S - $Sb(1^3)$	93.85(39)	
$Pb(5^7)$ - S - $Pb(3^1)$	101.46(42)	
$Pb(5^7)$ - S - $Pb(2^7)$	97.06(53)	
$Pb(5^7)$ - S - $Sb(4^3)$	164.76(63)	
$Pb(4^5)$ - S - $Sb(1^3)$	93.37(40)	
$Sb(1^3)$ - S - $Pb(3^1)$	84.77(55)	
$Pb(3^1)$ - S - $Pb(2^7)$	90.27(44)	
$Pb(2^7)$ - S - $Pb(4^5)$	87.86(49)	
$Sb(1^3)$ - S - $Pb(2^7)$	168.72(66)	
$Pb(3^1)$ - S - $Pb(4^5)$	160.22(57)	
$Sb(4^3)$ - S - $Pb(4^5)$	86.49(29)	
$Sb(4^3)$ - S - $Sb(1^3)$	71.35(38)	
$Sb(4^3)$ - S - $Pb(3^1)$	74.23(48)	
$Sb(4^3)$ - S - $Pb(2^7)$	97.57(36)	

S(7)

$Sb(2^7)$ - S - $Pb(1^3)$	91.69(52)	degrees
$Sb(2^7)$ - S - $Pb(2^7)$	96.53(72)	
$Sb(2^7)$ - S - $Pb(3^1)$	100.29(44)	
$Sb(2^7)$ - S - $Pb(4^1)$	103.41(46)	
$Pb(1^3)$ - S - $Pb(2^7)$	84.18(45)	
$Pb(2^7)$ - S - $Pb(3^1)$	96.53(72)	
$Pb(3^1)$ - S - $Pb(4^1)$	85.30(55)	
$Pb(4^1)$ - S - $Pb(1^3)$	96.51(40)	
$Pb(3^1)$ - S - $Pb(1^3)$	167.15(38)	
$Pb(2^7)$ - S - $Pb(4^1)$	160.01(56)	

S(8)

$Sb(3^1)$ - S - $Pb(1^3)$	90.32(67)	degrees
$Sb(3^1)$ - S - $Pb(4^3)$	102.67(44)	
$Sb(3^1)$ - S - $Pb(2^1)$	100.44(43)	
$Pb(1^3)$ - S - $Pb(4^3)$	106.51(43)	
$Pb(4^3)$ - S - $Pb(2^1)$	90.94(61)	
$Pb(2^1)$ - S - $Pb(1^3)$	157.06(46)	

TABLE 15
(continued)

Sulfur-Metal Bond Distances and Angles

B. Bond Angles

S(9)

$Sb(4^1)$ - S - $Pb(1^1)$	101.74(42)	degrees
$Sb(4^1)$ - S - $Sb(4^3)$	74.92(46)	
$Sb(4^1)$ - S - $Pb(2^1)$	101.12(47)	
$Pb(1^1)$ - S - $Pb(2^1)$	96.25(64)	
$Pb(2^1)$ - S - $Sb(4^3)$	171.04(48)	
$Sb(4^3)$ - S - $Pb(1^1)$	76.97(34)	

S(10)

$Pb(4^3)$ - S - $Sb(3^1)$	86.84(36)	degrees
$Pb(4^3)$ - S - $Pb(5^1)$	95.70(63)	
$Pb(4^3)$ - S - $Sb(1^6)$	100.27(53)	
$Pb(4^3)$ - S - $Sb(2^5)$	92.70(37)	
$Pb(4^3)$ - S - $Pb(5^6)$	148.32(62)	
$Sb(3^1)$ - S - $Sb(1^6)$	170.25(87)	
$Pb(5^1)$ - S - $Sb(2^5)$	162.72(65)	
$Sb(3^1)$ - S - $Pb(5^1)$	85.22(38)	
$Pb(5^1)$ - S - $Sb(1^6)$	100.56(62)	
$Sb(1^6)$ - S - $Sb(2^5)$	92.73(51)	
$Sb(2^5)$ - S - $Sb(3^1)$	80.19(49)	
$Pb(5^6)$ - S - $Sb(3^1)$	65.76(36)	
$Pb(5^6)$ - S - $Pb(5^1)$	97.42(33)	
$Pb(5^6)$ - S - $Sb(1^6)$	105.46(50)	
$Pb(5^6)$ - S - $Sb(2^5)$	68.16(45)	

S(11)

$Pb(3^6)$ - S - $Sb(2^4)$	91.13(35)	degrees
$Pb(3^6)$ - S - $Pb(5^4)$	92.94(36)	
$Pb(3^6)$ - S - $Pb(3^1)$	101.63(47)	
$Pb(3^6)$ - S - $Sb(1^3)$	97.20(66)	
$Pb(3^6)$ - S - $Sb(2^3)$	152.91(65)	
$Sb(2^4)$ - S - $Pb(5^4)$	81.20(49)	
$Pb(5^4)$ - S - $Pb(3^1)$	89.39(42)	
$Pb(3^1)$ - S - $Sb(1^3)$	94.56(55)	
$Sb(1^3)$ - S - $Sb(2^4)$	92.42(42)	
$Sb(2^3)$ - S - $Sb(2^4)$	69.09(46)	
$Sb(2^3)$ - S - $Pb(5^4)$	66.61(41)	
$Sb(2^3)$ - S - $Pb(3^1)$	95.96(40)	
$Sb(2^3)$ - S - $Sb(1^3)$	101.80(35)	
$Pb(3^1)$ - S - $Sb(2^4)$	164.55(73)	
$Pb(5^4)$ - S - $Sb(1^3)$	168.13(64)	

TABLE 16

Sulfur-Sulfur Contact Distances

Pb(1)

S(7^7) - S(9^3)	4.306(28) Å	2x
S(9^3) - S(3^5)	3.356(22)	2x
S(3^5) - S(8^5)	3.662(29)	2x
S(8^5) - S(7^7)	3.900(21)	2x
S(7^7) - S(8^7)	3.989(20)	2x
S(7^7) - s(3^7)	3.615(20)	2x
S(9^3) - S(3^7)	4.262(18)	2x
S(9^3) - S(9^1)	3.817(27)	
S(8^5) - S(8^7)	3.405(19)	

Pb(2)

S(4^1) - S(6^7)	3.828(23) Å
S(4^1) - S(7^7)	3.563(30)
S(4^1) - S(9^1)	3.817(18)
S(4^1) - S(8^1)	3.863(17)
S(6^7) - S(7^7)	4.089(21)
S(7^7) - S(9^1)	4.301(28)
S(9^1) - S(8^1)	4.134(20)
S(8^1) - S(6^7)	4.035(28)
S(1^1) - S(2^7)	3.297(14)
S(2^7) - S(7^7)	4.258(16)
S(2^7) - S(9^1)	3.694(26)
S(1^1) - S(8^1)	4.253(33)
S(1^1) - S(6^7)	3.602(12)

Pb(3)

S(11^6) - S(7^1)	3.810(18) Å
S(11^6) - S(6^1)	3.774(18)
S(11^6) - S(11^1)	3.634(31)
S(11^6) - S(5^7)	3.523(29)
S(7^1) - S(6^1)	4.089(21)
S(6^1) - S(11^1)	4.027(27)
S(11^1) - S(5^7)	4.097(20)
S(5^7) - S(7^1)	4.266(27)
S(3^7) - S(9^1)	3.356(22)
S(7^1) - S(9^1)	4.141(23)
S(11^1) - S(3^7)	3.724(23)
S(3^7) - S(5^7)	3.731(16)

TABLE 16
(continued)

Sulfur-Sulfur Contact Distances

Pb(4)

S(10^2) - S(6^5)	3.669(30) Å	
S(10^2) - S(8^3)	3.790(18)	
S(10^2) - S(5^7)	3.523(23)	
S(10^2) - S(7^1)	3.681(18)	
S(6^5) - S(8^3)	4.035(28)	
S(8^3) - S(7^1)	3.900(21)	
S(7^1) - S(5^7)	4.266(27)	
S(5^7) - S(6^5)	4.158(21)	
S(6^5) - S(1^1)	3.602(12)	
S(5^7) - S(2^7)	3.630(21)	
S(7^1) - S(2^7)		
S(1^1) - S(2^7)	3.297(14)	

Pb(5)

S(6^7) - S(10^1)	3.669(30) Å	
S(6^7) - S(4^1)	3.828(22)	
S(6^7) - S(11^4)	3.774(18)	
S(6^7) - S(5^6)	3.698(18)	
S(10^1) - S(4^1)	4.440(20)	
S(4^1) - S(11^4)	4.226(27)	
S(11^4) - S(5^6)	4.097(20)	
S(5^6) - S(10^1)	3.897(28)	
S(10^6) - S(3^6)	3.950(21)	
S(10^6) - S(4^1)	3.933(22)	
S(10^6) - S(10^1)	4.221(23)	
S(3^6) - S(11^4)	3.724(23)	
S(5^6) - S(3^6)	3.731(15)	

Sb(1)

S(5^2) - S(10^6)	3.523(23)
S(5^2) - S(11^3)	3.523(29)
S(5^2) - S(6^3)	3.698(18)
S(5^2) - S(5^1)	3.640(24)
S(10^6) - S(11^3)	3.823(21)
S(11^3) - S(6^3)	4.027(27)
S(6^3) - S(5^1)	4.158(21)
S(5^1) - S(10^6)	3.897(28)
S(4^1) - S(2^1)	3.974(28)
S(2^1) - S(5^1)	3.630(21)
S(2^1) - S(6^3)	4.127(16)
S(4^1) - S(10^6)	3.933(22)
S(4^1) - S(11^3)	3.807(16)

TABLE   16
(continued)

Sulfur-Sulfur Contact Distances

Sb(2)

S(7^7) - S(4^1)	3.563(30)
S(7^7) - S(3^5)	3.615(22)
S(7^7) - S(10^5)	3.681(18)
S(7^7) - S(11^4)	3.810(18)
S(4^1) - S(3^5)	3.861(20)
S(3^5) - S(10^5)	3.960(29)
S(10^5) - S(11^4)	3.822(21)
S(11^4) - S(4^1)	3.807(16)
S(11^3) - S(4^2)	4.226(27)
S(11^3) - S(4^1)	3.807(16)
S(11^3) - S(3^5)	3.724(23)
S(4^2) - S(10^5)	3.933(22)
S(4^2) - S(11^4)	3.807(16)

Sb(3)

S(8^1) - S(3^1)	3.662(30)
S(8^1) - S(2^1)	3.525(23)
S(8^1) - S(4^1)	3.863(17)
S(8^1) - S(10^1)	3.790(18)
S(3^1) - S(2^1)	3.620(20)
S(2^1) - S(4^1)	3.974(28)
S(4^1) - S(10^1)	4.440(20)
S(10^1) - S(3^1)	3.960(28)
S(5^1) - S(10^6)	3.897(28)
S(5^1) - S(3^1)	3.731(16)
S(5^1) - S(2^1)	3.630(21)
S(10^6) - S(4^1)	3.933(22)
S(10^6) - S(10^1)	4.221(23)

Sb(4)

S(9^1) - S(2^1)	3.789(29)
S(9^1) - S(1^3)	3.664(32)
S(9^1) - S(9^3)	3.817(27)
S(9^1) - S(4^1)	3.817(18)
S(2^1) - S(1^3)	3.297(14)
S(1^3) - S(9^3)	3.664(14)
S(4^1) - S(2^1)	3.974(28)
S(6^3) - S(2^1)	4.127(16)
S(6^3) - S(1^3)	3.602(12)
S(3^5) - S(9^3)	3.356(22)
S(3^5) - S(4^1)	3.861(20)

FIGURE 6

(010) Projection Semseyite
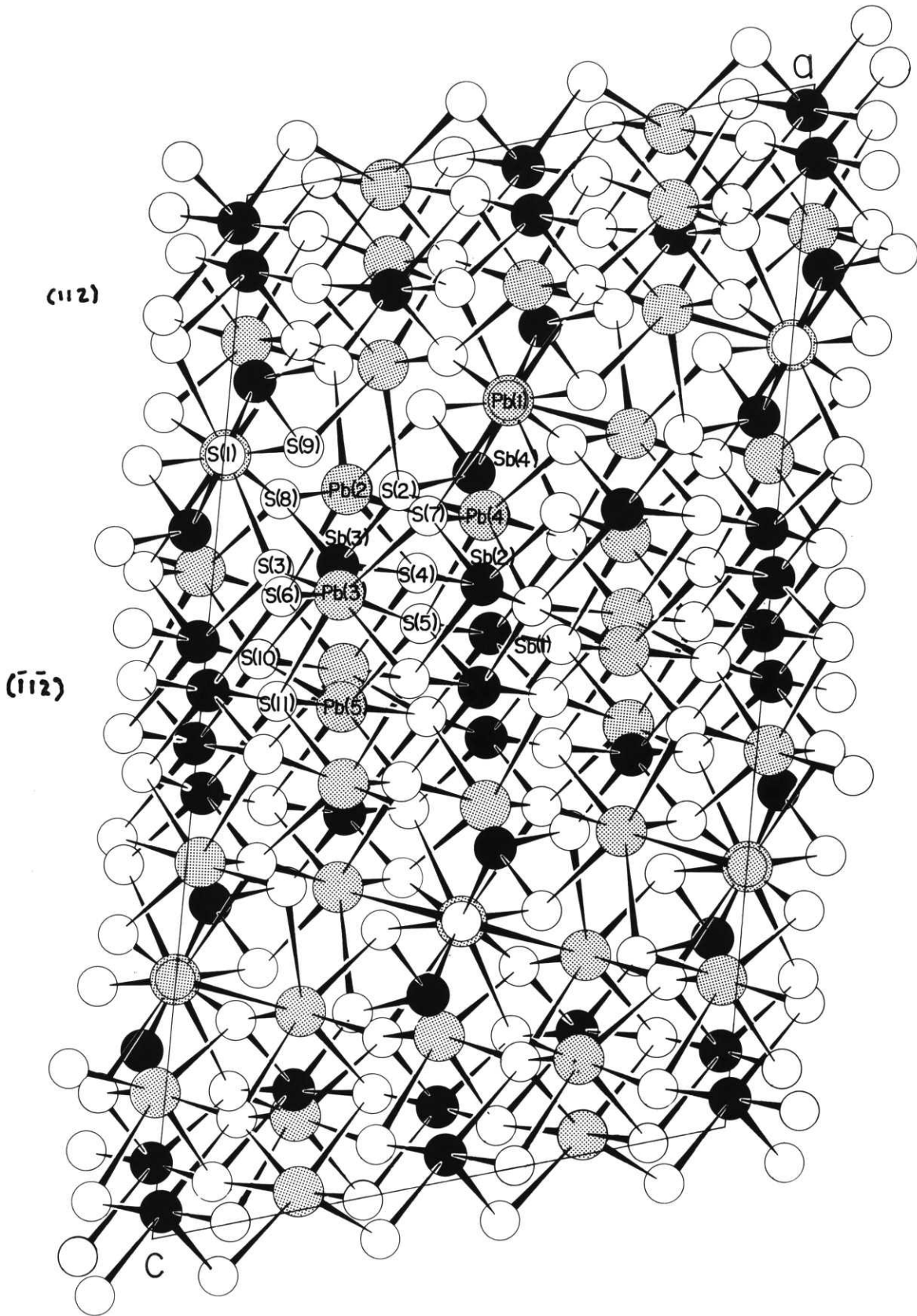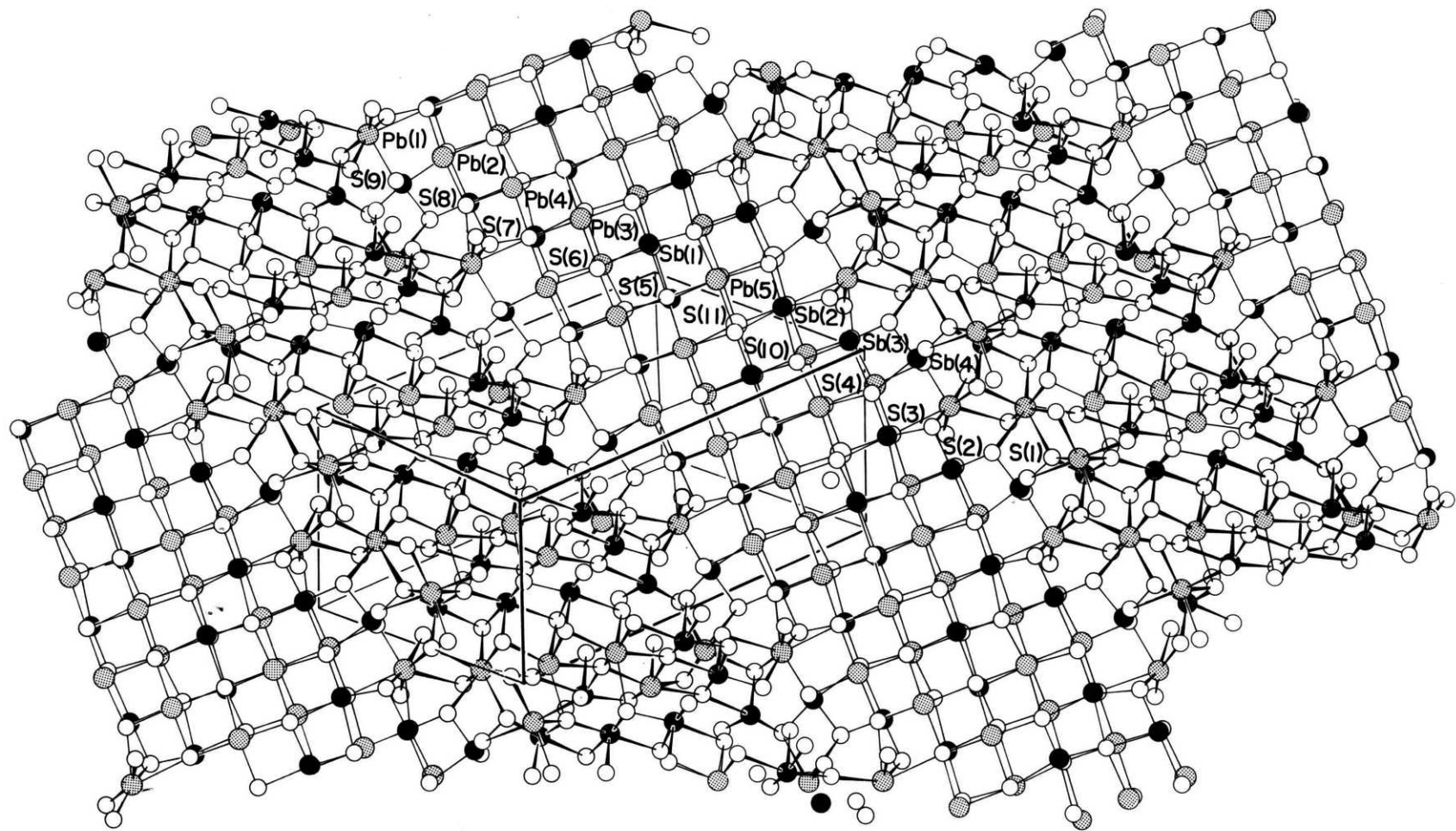
(112) Projection Semseyite

FIGURE 7

Pb(1), Pb(4), Sb(4), Sb(2), and Sb(1). The chains at x = .25 and .75 are predominately lead 'chains' with Pb(2), Pb(3), Pb(5) and Sb(3). The sulfur atoms provide a chain-like formation that joins the lead and antimony 'chains'. Between the Pb(1)'s, on the two-fold positions, the density of bonds can be seen to be quite thick. However, in the immediate vicinity of z =.25, 0.75 (x=0 to 1) the density of bonds appears to be quite sparse. This combination of an area of thick bonding with a region of thin bonding suggests that the structure might be described as sheets or slabs joined to one another at points of relatively sparse bonding. The (010) projection has indicated upon it (Figure 6) regions designated as (112) and ($\bar{1}1\bar{2}$). This designates the plane to which the slab-like unit is parallel. The slabs in the two orientations are related by the two-fold rotation axis (at Pb(1)) parallel to b.

For further study, the structure was projected onto (112), the plane of one of the two slabs).(Figure 7) Here there is a region which resembles a rock-salt type configuration bordered by what seems to be a jumbled mess. This confusion is merely the projection of the second slab parallel to ($\bar{1}1\bar{2}$). Notice that the rock-salt-like area is terminated by the lead atoms (Pb(1)) and the sulfur atoms(S(1)) in the position of two-fold symmetry. The slab is composed of two levels which are related by a center of inversion. A diagonal line of metal atoms will be noticed running along [110] of the PbS-like cells on either level. The line starts with Pb(1) and is terminated by Sb(4). Running from Pb(1) to Sb(4) the atoms are Pb(1), Pb(2), Pb(4), Pb(3), Sb(1), Pb(5), Sb(2), Sb(3),

and Sb(4). Parallel to this diagonal line of metals is a line of
sulfur atoms again running along the [110] of a PbS cell. Start-
ing with the sulfur on the two-fold special position, the line is
S(1), S(2), S(3), S(4), S(10),S(11), S(5), S(6), S(7), S(8), and
S(9). These two chains, all on one level of the slab, are the
complete asymmetric unit of the structure. The rest of the slab
may be generated by the center of inversion and the C centering
translation. The C centering translation appears on the (112)
projections as the distance and direction between equivalent Pb(1)
atoms on the same level (i.e. top or bottom of the slab, not mixed).

The coordination polyhedra can be visualized very easily in
the (112) projection. (It should be noted that atoms not lying in
the PbS-like slab but rather in an adjacent one are not shown for
the rock-salt portion. Therefore, with the exception of Pb(1) and
Sb(4), the polyhedra will not be complete. Thus the sixth and
seventh neighbors for all the other atoms represent bonding between
the adjacent (112) slabs.) It can be seen that three of the four
lead atoms in the general position, Pb(3), Pb(4), and Pb(5), share
the four equatorial edges with polyhedra in the same level. The
exception Pb(2), which is near the edge of the slab, shares only
three of these edges. Like-wise all four general position lead
atoms share all four of their nearest apex edges with polyhedra in
the adjacent level. Similarly the antimony polyhedra can be un-
derstood. Sb(1) shares four basal edges and four apical edges;
Sb(2) shares three basal and four apical edges. Sb(3) and Sb(4)

which are near the edge of the slab, share fewer elements with the other polyhedra. Sb(3) shares two basal and three apical edges and one corner while Sb(4) shares only corners.

Visualization of the structure in three dimensions is not difficult if one abandons the traditional 'ball and stick' approach to adopt the slab, or as it is known locally, the 'kite' method. Take one 'rock-salt-like slab' parallel to (112) and imagine it as a unit which is two atoms thick. This slab is mounted in the cell by anchoring it at the two-fold axes. The slab itself extends indefinately along [1$\bar{1}$0]. It is repeated by the b-axis translation and rotated by the two-fold axes to form ($\bar{1}$1$\bar{2}$) slabs which are equivalent. Thus semseyite is a stack of (112) slabs joined to and alternating with ($\bar{1}$1$\bar{2}$) slabs at the lead and sulfur atoms, Pb(1) and S(1). The observed perfect (112) cleavage is explained by the fact that only a few long weak bonds bind the stack of (112) slabs together. Bonding within a single (112) slab is much stronger. Also it should be noted that the sulfurs with tetrahedral coordination all occur along the edges of the slab, while the higher coordinated sulfurs occur in the center of the slab.

Thus semseyite, the end member of the plagionite group, is seen to be a series of 'rock-salt-like' slabs two atoms thick connected in the c direction by a lead and sulfur atom at the special two-fold positions. The slabs are extended indefinjtely along [1$\bar{1}$0] and are 'stacked' by the b translation.

Chapter VII

Semseyite, Stibnite, Galena, and Plagionite

Since only one other lead-antimony sulfosalt structure, plagionite, has been solved, the number of other related minerals available for comparison to the structure of semseyite is some- what limited. However, the coordination geometry of the metals in semseyite can be compared with that in stibnite, Sb_2S_3, and galena, PbS.

Recently Nowacki and Bayliss(1971) refined the structure of stibnite and calculated more precise bond distances. They found that antimony is both five-coordinated and three-coordinated. The former scheme is similar to that known for the bismuth sulfosalts while the latter is characteristic of arsenic sulfosalts. The five-coordinated Sb atom has one near sulfur neighbor at 2.455(3)A°, four intermediate at 2.678(2) A° and 2.854 A°. The three-coordi- nated antimony atom has a very near sulfur neighbor at 2.521(3) A° then two at a distance of 2.539(2) A°. In semseyite three of the antimony atoms, Sb(1), Sb(2), and Sb(3), are decidely five-coordi- nated. The fourth, Sb(4), is three-coordinated. Considering, the five-coordinated antimony atoms, the average equatorial bond distances are 2.766 A° for stibnite but slightly larger values of 2.821 A°(Sb(1)), 2.818 A° (Sb(2)) and 2.819 A° (Sb(3)) in semseyite. The distances to the apical sulfur are slightly shorter for two of the antimony atoms. Sb(2) and Sb(3) have apical distances of 2.395 A° and 2.378 A° respectively. This is nearly 0.05 A° shorter than the similar stibnite distance, 2.455 A° or the apical distance

for Sb(1), 2.441 A°. It should be noted that although these antimony atoms in semseyite are not located on a mirror plane as they are in stibnite, their equatorial sulfur neighbors come in distinct, nearly equal, pairs, i.e. the coordination is [1+2+2]. For Sb(1) the first pair is 2.528 and 2.570 A°, and the second pair 3.085 and 3.100 A°. For Sb(2) the pairs are 2.553 - 2.556 A° and 3.053 - 3.102 A° and for Sb(3) 2.470 - 2.552 A° and 3.123 - 3.134 A°. The fourth antimony atom, Sb(4), is three- coordinated. The average bond distance is 2.465 A°, nearly 0.1 A° shorter than the average 2.533 A° value of stibnite. Although five neighbors can be located for Sb(4), they do not conform to the 'pair-arrangement' described for the other three Sb atoms and stibnite. Sb(4) can have one pair of equatorial sulfur atoms at 2.492 - 2.506 A° but the second 'pair' is a 3.157 - 3.454 A°. Therefore it must be concluded that Sb(4) has a decidedly different configuration from the other three.

The obvious comparison to make is that of the lead polyhedra in semseyite with galena, PbS. For galena the Pb-S distance for six-coordinate lead is 2.965 A°. Two of the semseyite lead polyhedra Pb(3) and Pb(4) have average six-coordinated distances of 2.971 and 2.970 A°. The five-coordinated Pb(5) has a shorter average distance - 2.895 A° while the seven and eight coordinated lead atoms, Pb(2) and Pb(1), have average distances of 3.023 and 3.021 A° respectively. Thus to within 0.06 A°, the average Pb-S distance in semseyite agrees with that in galena. However, it should be noticed that within each coordination polyhedra bond distances

range from 2.854 to 3.564 A° for Pb(1), 2.820 to 3.339 A°, Pb(2), 2.782 to 3.208 A°, Pb(3), 2.789 to 3.270 A°, Pb(4), and 2.610 to 3.098 A°, Pb(5). Thus while the overall view of the structure reveals galena-like coordination for the lead atoms (see (112) projection, Figure 7), the details of the coordination are different.

Comparison can also be made of the structure of semseyite to that of her sister mineral plagionite. In both minerals there are four independent antimony atoms. Three Sb atoms in each structure are five-coordinated and one, Sb(4), is three-coordinated. The two sets of polyhedra (i.e. plagionite and semseyite) are remarkably similar. Small differences arise in apical bond distances - semseyite is generally slightly shorter (∿.04 A°) - and the second 'pair' of equatorial sulfurs - semseyite is generally equal or longer (∿.10 A°). This may be rationalized as the effect of the addition of two lead atoms and two sulfur atoms. Considering the (112) projection, the apical bond distance measures the thickness of the 'slab', while the equatorial distances represent distances within one level of the slab. Thus comparing the (112) projections of semseyite (Figure 7) and plagionite (Figure 8) it can be seen that while the thickness of the 'slab' does not change the width does - thereby slightly distorting the equatorial distances.

Before comparing the lead polyhedra, it is necessary to decide which two lead atoms have been added to plagionite to form semseyite. Close scrutiny of the (010) projections of semseyite and plagionite (Figure 6 and Figure 9) revealed that Pb(1), Pb(2),
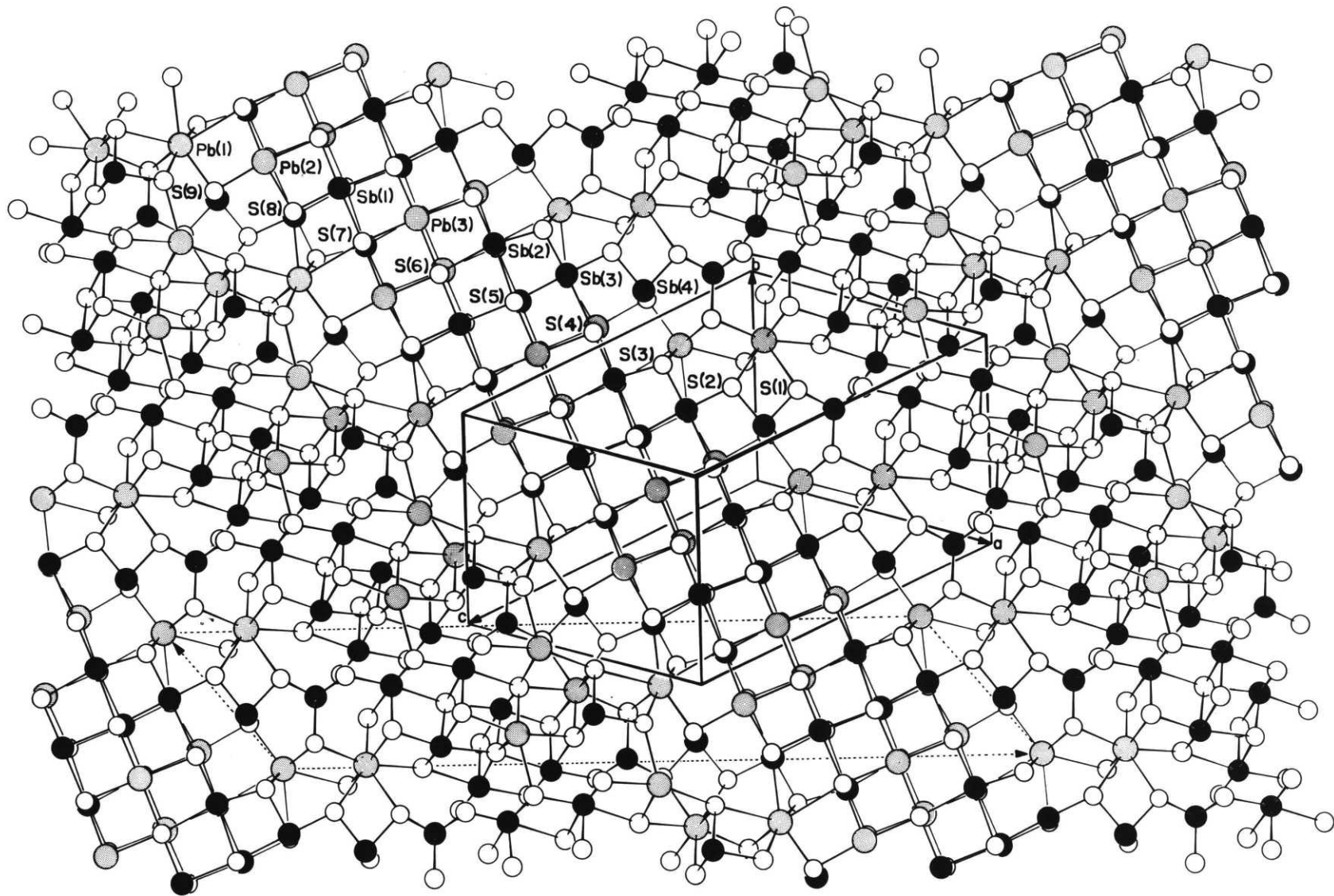
(112) Projection Plagionite

FIGURE 8

FIGURE 9   85

(010) Projection Plagionite
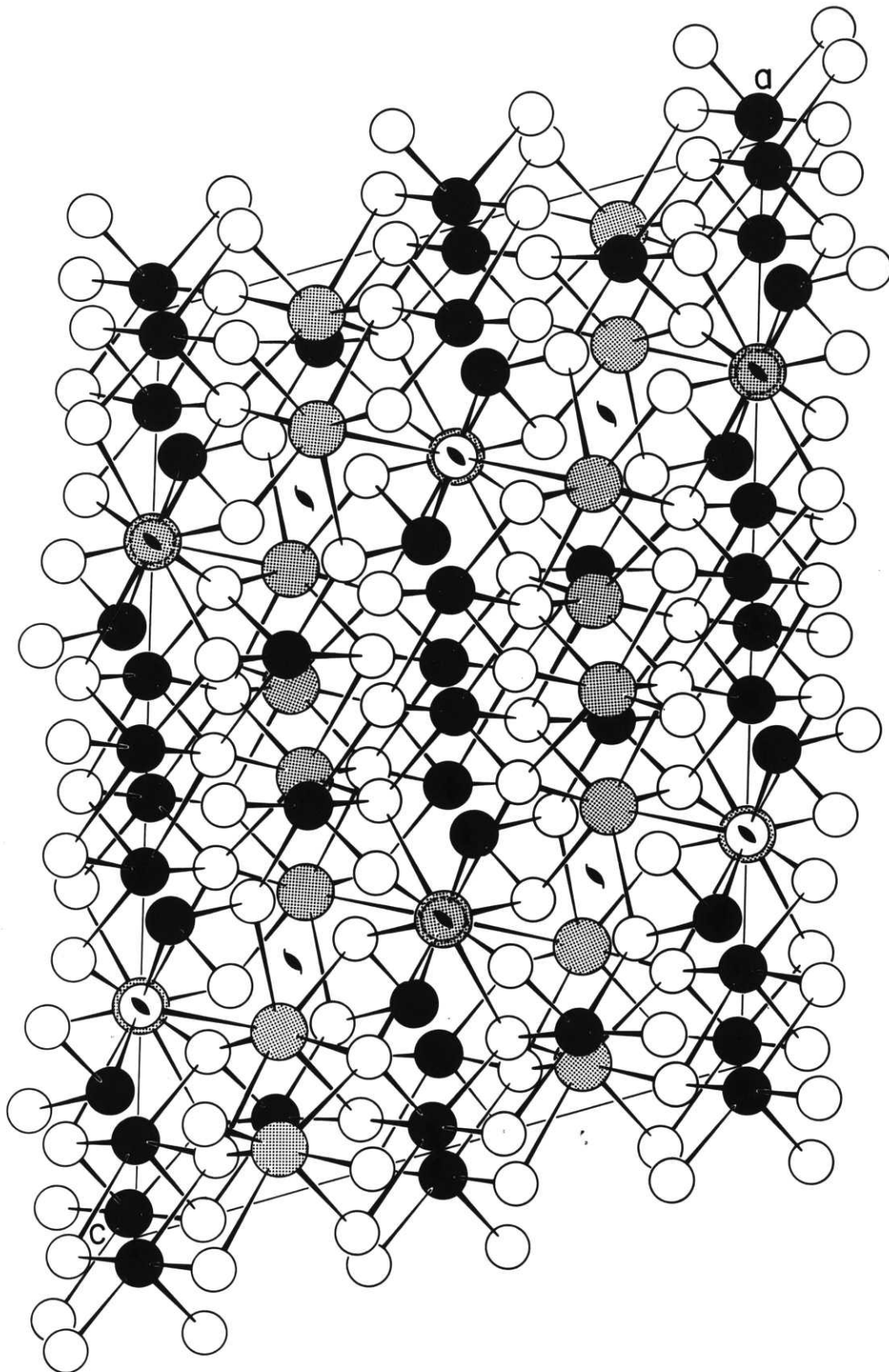
and Pb(3) were virtually identical. However, Pb(4) and S(10) and
Pb(5) and S(11) have no counterparts in palgionite. The variations
in bond distances are, as a rule, within the error of the measure-
ments for the lead polyhedra occuring in both structures. However,
Pb(1) in semseyite, the lead atom in equipoint 4e, is more closely
coordinated by its fifth and sixth and seventh and eighth neighbors
by nearly 0.1 A° than Pb(1) in plagionite. A visual comparison of
the antimony polyhedra and three lead polyhedra of both semseyite
and plagionite is presented in Figure 10.

Comparing the (112) slabs of both plagionite and semseyite,
one finds that plagionite has nearly flat levels of the slabs. The
maximum variation is only 0.6 A°. In semseyite, however, the levels
of the slab approximate hills and valleys with a difference within
one line of the level being as much as 2.0 A°. The thickness of
the two slabs is very similar as it represents Sb-S and Pb-S
apical bonding.

It is most interesting to consider how plagionite can be
"made" from semseyite. The clearest way to see this is to study
the (010) projections. Consider Figure 11, the (010 projection
of semseyite. The halftone region represents the portion of the
structure that is similar to plagionite. The white area represents
the 'new' region. If the 's-shaped' region is removed, and the
bonds broken along the dashed lines, the two portions will collapse
together removing the void. This is plagionite. The direction of
the collapse in not exactly [001] but rather the direction of

FIGURE 10

87

SEMSEYITE

PLAGIONITE

FIGURE 10 (cont.)   88
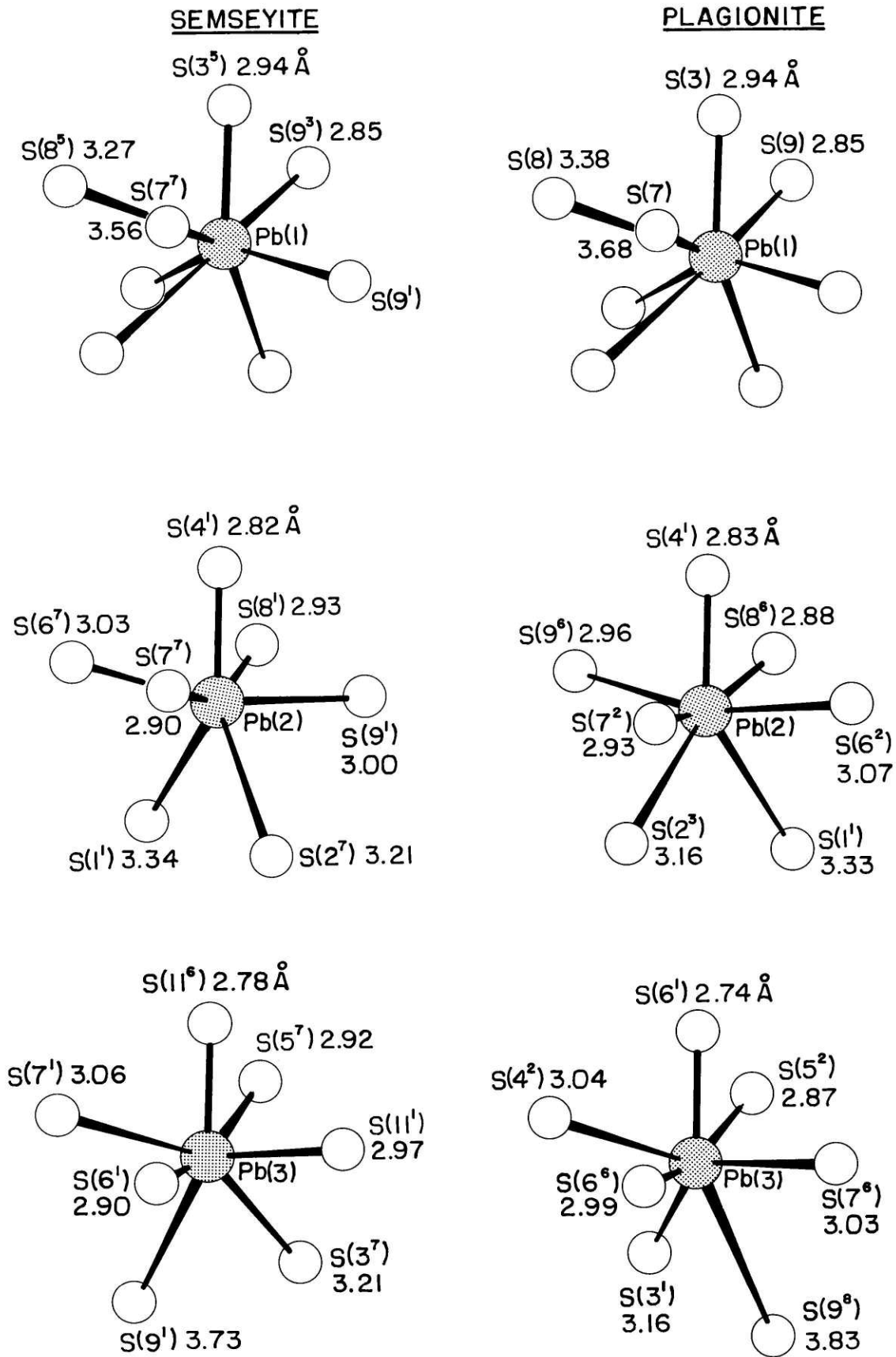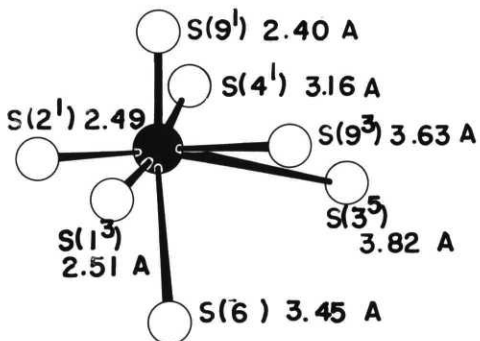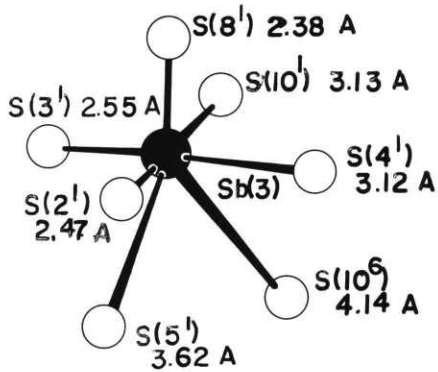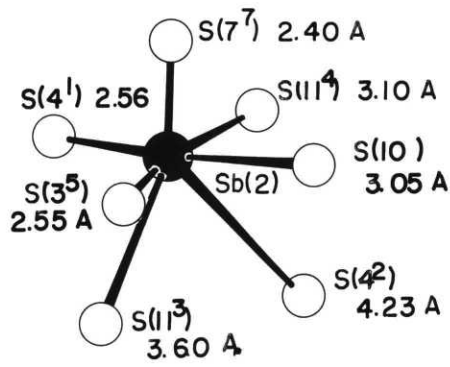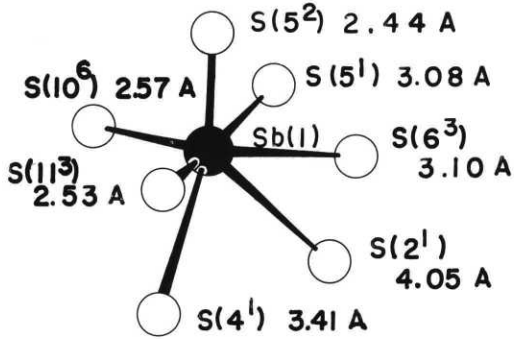
SEMSEYITE
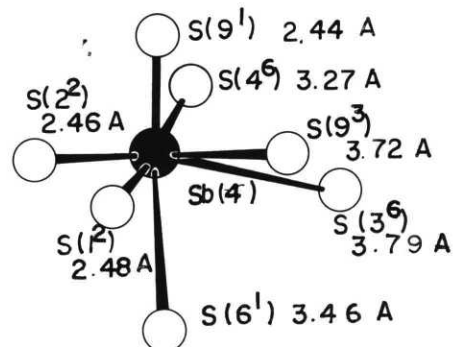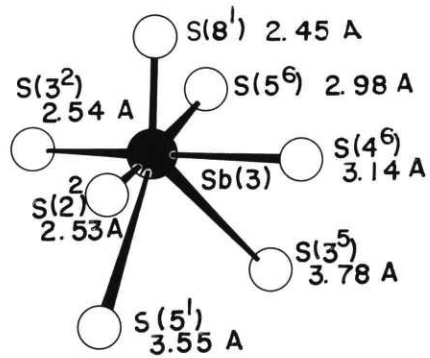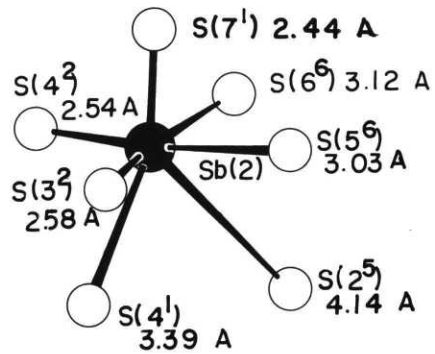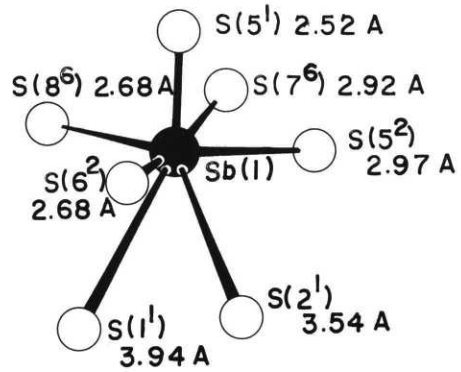
PLAGIONITE

FIGURE 11
"Making" Plagionite from Semseyite
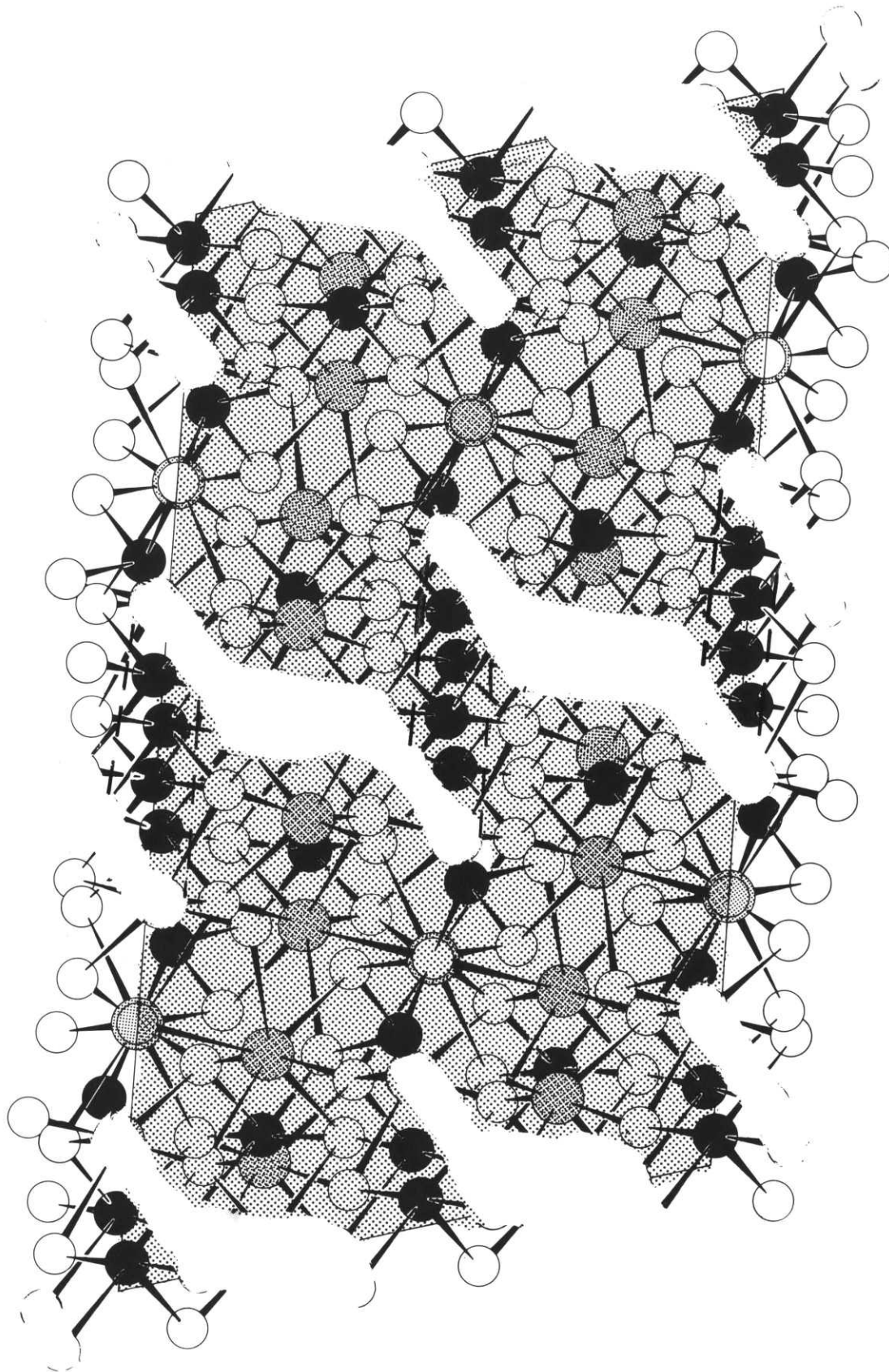
c sin β.   Thus as Jambor (1969) predicted c sin β rather than c

shows a linear increase as one goes from plagionite to semseyite.

Chapter VIII

The Homologous Series $Pb_{3+2n}Sb_8S_{15+2n}$

It is believed that the plagionite group - fülöppite, plagionite, heteromorphite, and semseyite - forms an homologous series. The series is represented by the general equation - $Pb_{3+2n}Sb_8S_{15+2n}$ - as proposed by Peacock and Nuffield (1945) and Jambor (1969). From the results of the previous chapter, this formulization may be rewritten as $(2n+1)PbS \cdot 4Sb_2S_3$. Alternatively this is better understood when written

$$2nPbS[PbSb_8S_{13}]$$

where the portion enclosed in brackets is invariant throughout the series. Jambor has shown (Figure 1 and Table 2) that the density of the minerals increases linearly with n as does c sin β. Table 17 presents the density figures and $\Delta(c \sin\beta)$ for the series. Thus in constructing the series we must look for a method that provides a density increase as well as the 2.3 A° increase in c sin β.

From the previous chapter we saw that plagionite could be 'made' from semseyite by removal of a s-shaped region in a compound type operation. Breaking this operation down into its two components, we find that we can remove Pb(4) and S(10) to get a thin sausage shaped region or remove Pb(5) and S(11) to obtain a fatter and shorter sausage. The first process is shown schematically in Figure 12. For addition - first you must cut the structure at z=.50 parallel to [100]. Then separate the

FIGURE 12
Addition Process 1

a.

b.

$\frac{1}{4}[100]$

c.

d.
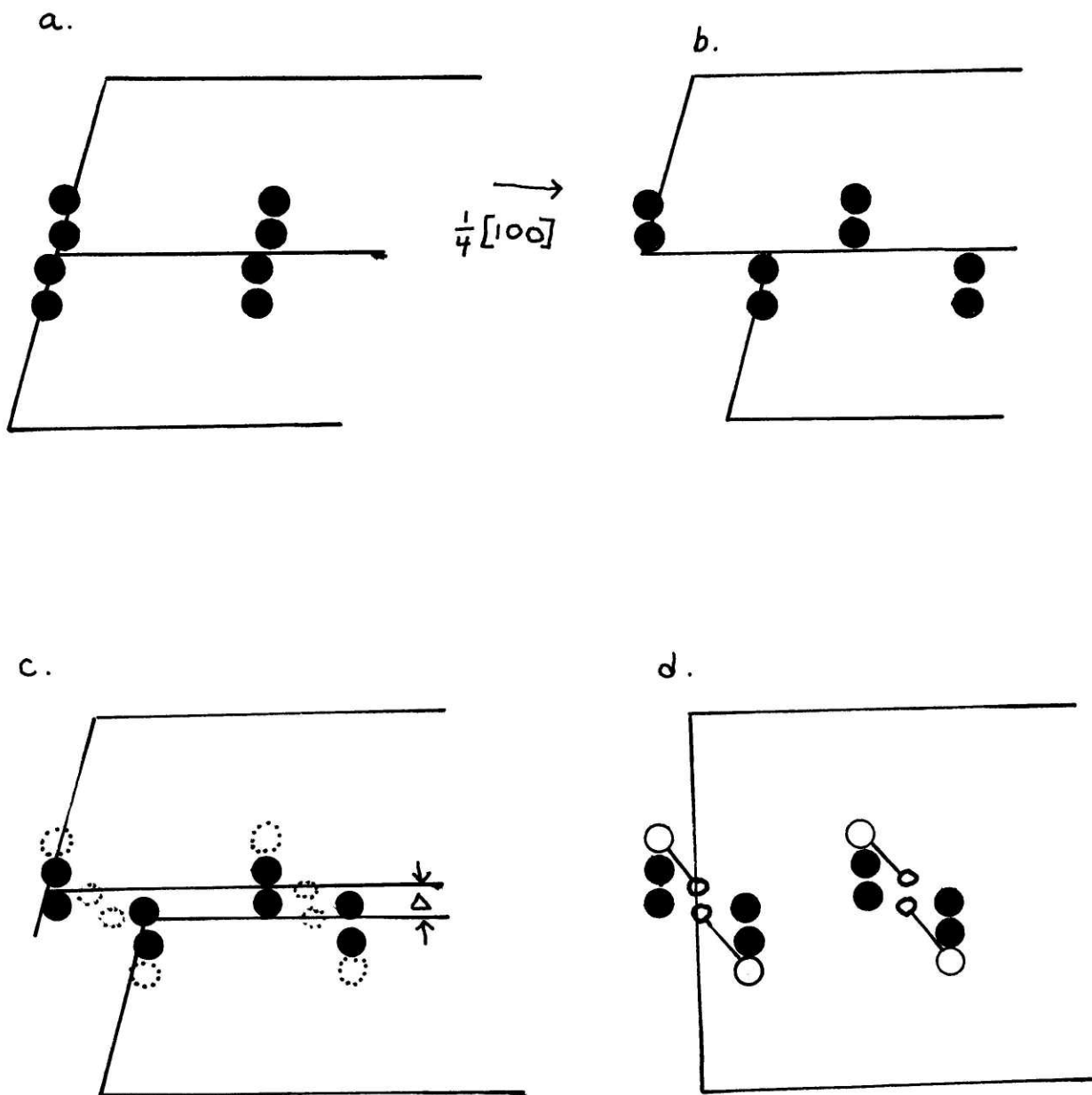
halves an Sb-Sb separation in the direction of c sin β(i.e. per-
pendicular to [100]). Then move the top half 0.25[100] relative
to the bottom half. Thus you have created a void into which you
can put a Pb and S. Note that you have disturbed only the inter-
ior region - not the area of the Pb(1), the lead on the 2-fold
position, and Sb(4), the trigonal Sb. If you connect the regions
of undisturbed area, you find you have a nearly orthogonal cell
characteristic of fülöppite and heteromorphite.

Similarly if you now take this structure as your starting
point, you can begin addition process 2 which is shown schematically
in Figure 13. Keeping the two Sb atoms together and repeating
the cutting, separating, and sliding processes of Process 1, we
arrive at an elliptical-type void into each two PbS can go. If
the edges of the undisturbed region are connected $\beta \sim 106°$ which
is typical of plagionite and semseyite.

Now if you calculate a typical Sb-Sb separation along c in
the a-c plane, you find that you must separate the two halves
approximately 1.15 A°(data from the Sb(1) - Sb(2) separation in
semseyite). This separation occurs twice in the length of c -
so the increase in c sin β is about 2.3 A°. This is exactly
what Jambor found. (Table 17)

The next item which requires explanation is the density
increase. It would appear that since we are increasing c that
addition of another atom or atoms would not produce a signifi-
cant density change. However, one must remember that we have
moved as Sb-Sb separation and therefore left what might be called

FIGURE 13
Addition Process 2
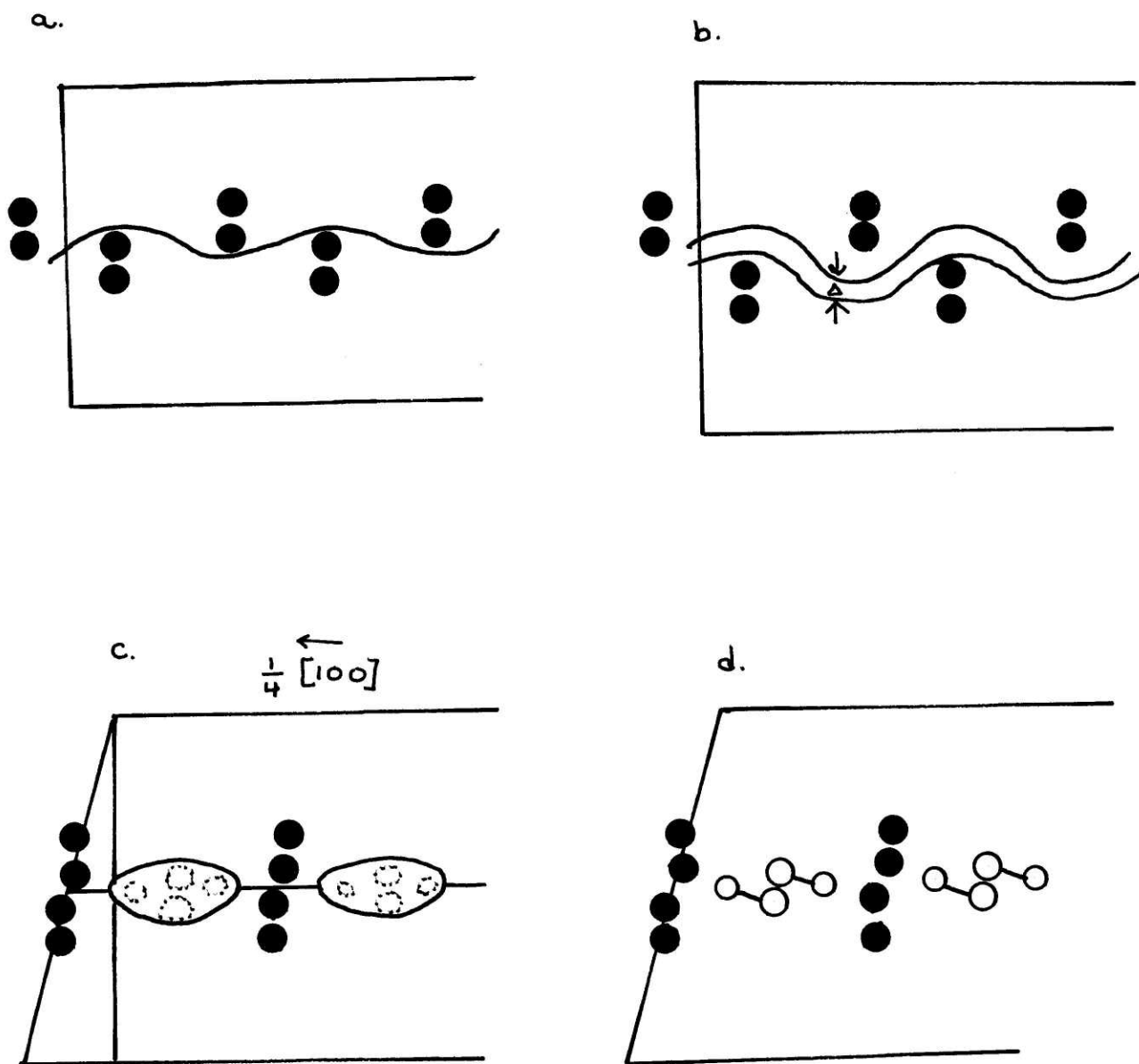
TABLE 17

Densities of the Plagionite Group and Changes of $c \sin \beta$

	ρ_{meas}	ρ_{calc}	$c \sin \beta$
fuloppite	5.21	5.22	
			2.3 A°
plagionite	5.58	5.54	
			2.3
hetero- morphite	5.86	5.73	
			2.3
semseyite	6.03	6.12	

a Sb hole. Into this vacant area we have put a lead. Therefore

into an area (or better volume) expecting a Sb we have placed

a Pb. Thus the progressive density increase arises.

Finally we must be concerned with how a Pb atom can occupy

a site previously occupied by Sb. In Figure 4 the polyhedra for

Sb were shown. If these are compared with those for Pb (Figure 3)

one can see the great similarity of the seven-coordinated atoms.

Thus while Sb only uses five neighboring S atoms as bonding part-

ners two other S atoms are in the near neighborhood to complete

a coordination polyhedra similar to that of seven coordinate Pb.

It is well to note that seven-coordinated bismuth in gladite

undergoes similar substitution by Pb in that lead-bismuth sulfo-

salt. (Kohatsu,I 1971)

Now that there is a predicted means of addition of PbS, it

is well to attempt to construct,at least in projection, the mem-

bers of the plagionite group. The subtraction process is easier

to show graphically so we shall first attempt to form hetero-

morphite from semseyite. Study.ing the unit cell constants we see

this involves moving from a cell with $\beta \sim 106°$ to $\beta \sim 90°$. There-

fore the subtraction process must be accomplished by the reverse

of the second addition process (Figure 13). Pb(5) and S(11) are

the atoms which are removed. The initial portion of the trans-

formation is shown in Figure 14. The predicted structure of

heteromorphite is shown in (010) projection in Figure 15.

Next plagionite can be formed from heteromorphite by the

reverse of the first addition process. Pb(4) and S(10) are removed

FIGURE 14
"Making" Heteromorphite from Semseyite
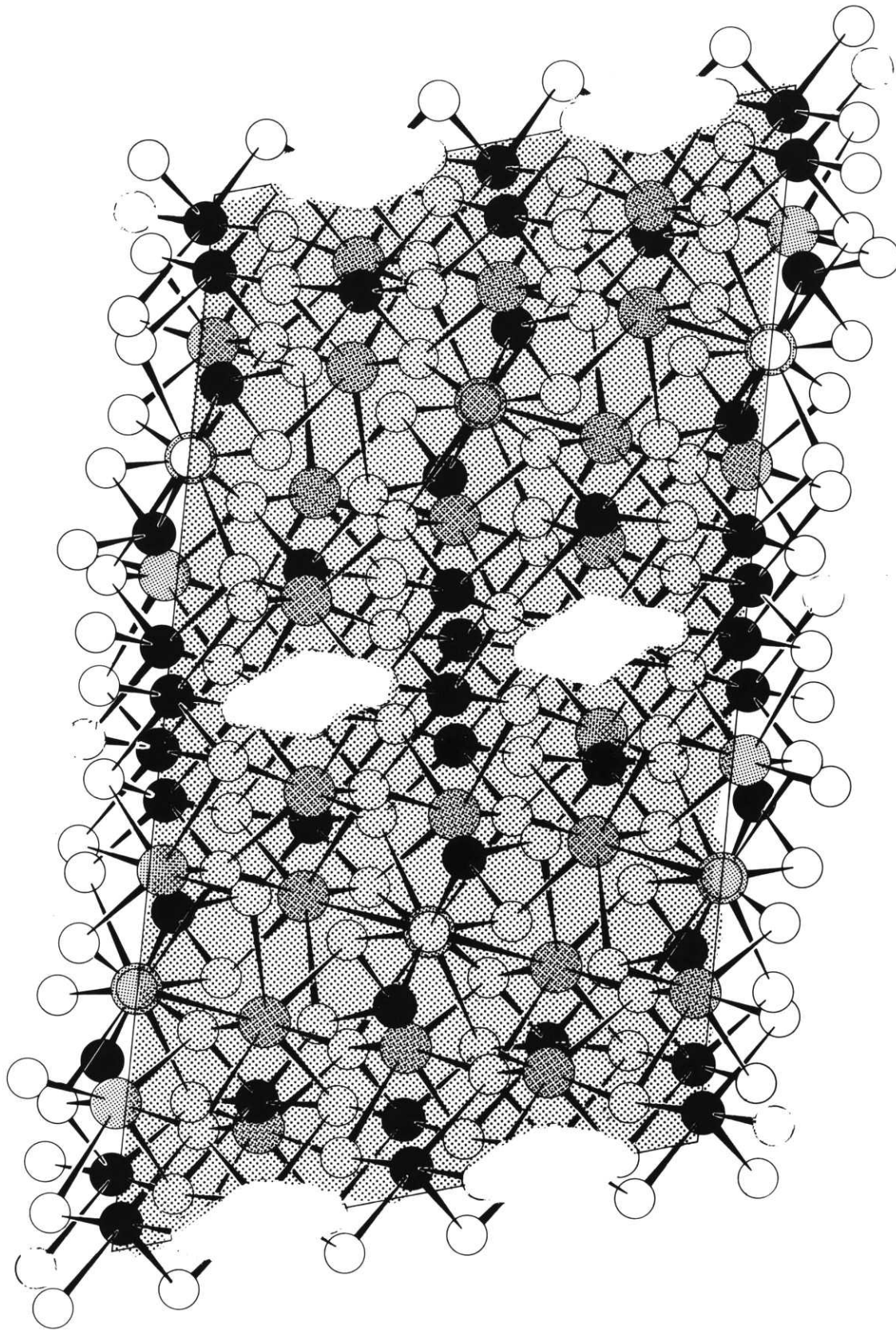
FIGURE 15
Predicted (010) Projection-Heteromorphite
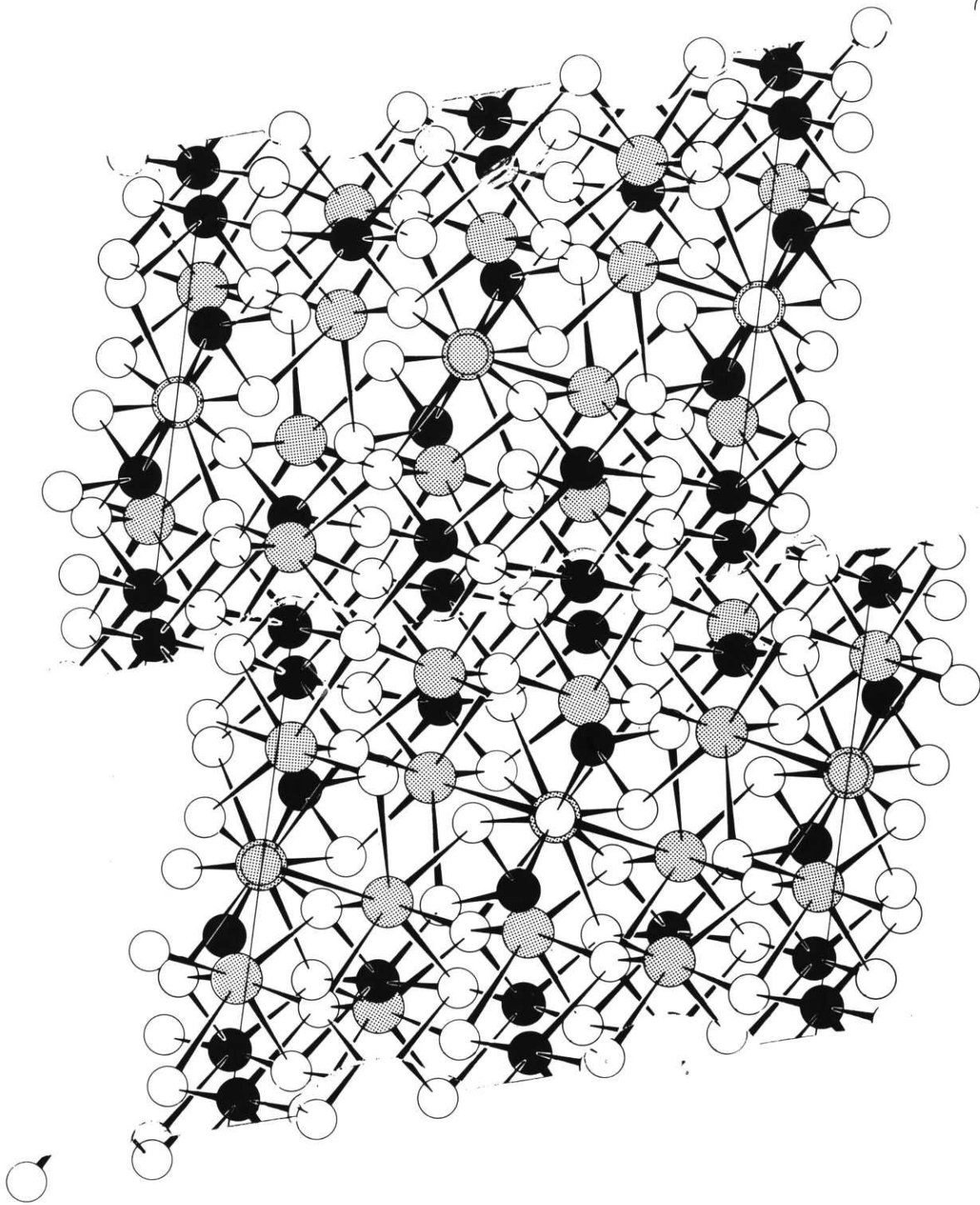
this time. The initial step of the process is shown in Figure 16.
The (010) projection of plagionite was presented in Figure 9.

Finally fülöppite can be made from plagionite. This requires
the removal of Pb(3) and S(5) and the reverse of the second ad-
dition process. The dissection of plagionite is shown in Figure 17
and the predicted structure in projection of fülöppite is shown
in Figure 18.

Looking back at the four structures, fuloppite, plagionite,
heteromorphite, and semseyite, we find that although the space
group has remained the same, the position of the lines of lead,
antimony and sulfur atoms has shifted relative to the inversion
centers. In the 90° compounds, fuloppite and heteromorphite,
the sulfur lines (or chains) pass through the inversion centers
at x=0,.25,.5,.75. The two lead and antimony 'chains' are now
quite similar and occur at x=.125,.375,625,.875. In the 106°
compounds, semseyite and plagionite, the lead and the antimony
'chains' pass through the inversion centers. Now, however,
there are two distinct types of 'chains' - the predominately
antimony chains at x=0,.5 and the lead ones at x=.25,.75. The
sulfur line now occupies the intermediate positions.

The structures as viewed on (112) appear relatively
similar. They are sketched schematically in Figure 19. Essentially
a PbS is removed from the interior region and the slab is collasped
to fill the void along the [110] of the PbS-like cell.

The next question that arises is can more Pb-S be added to
continue the group from semseyite to form para-heteromorphite and
para-semseyite. Adding PbS to semseyite requires the first type

FIGURE 16
"Making" Plagionite from Heteromorphite
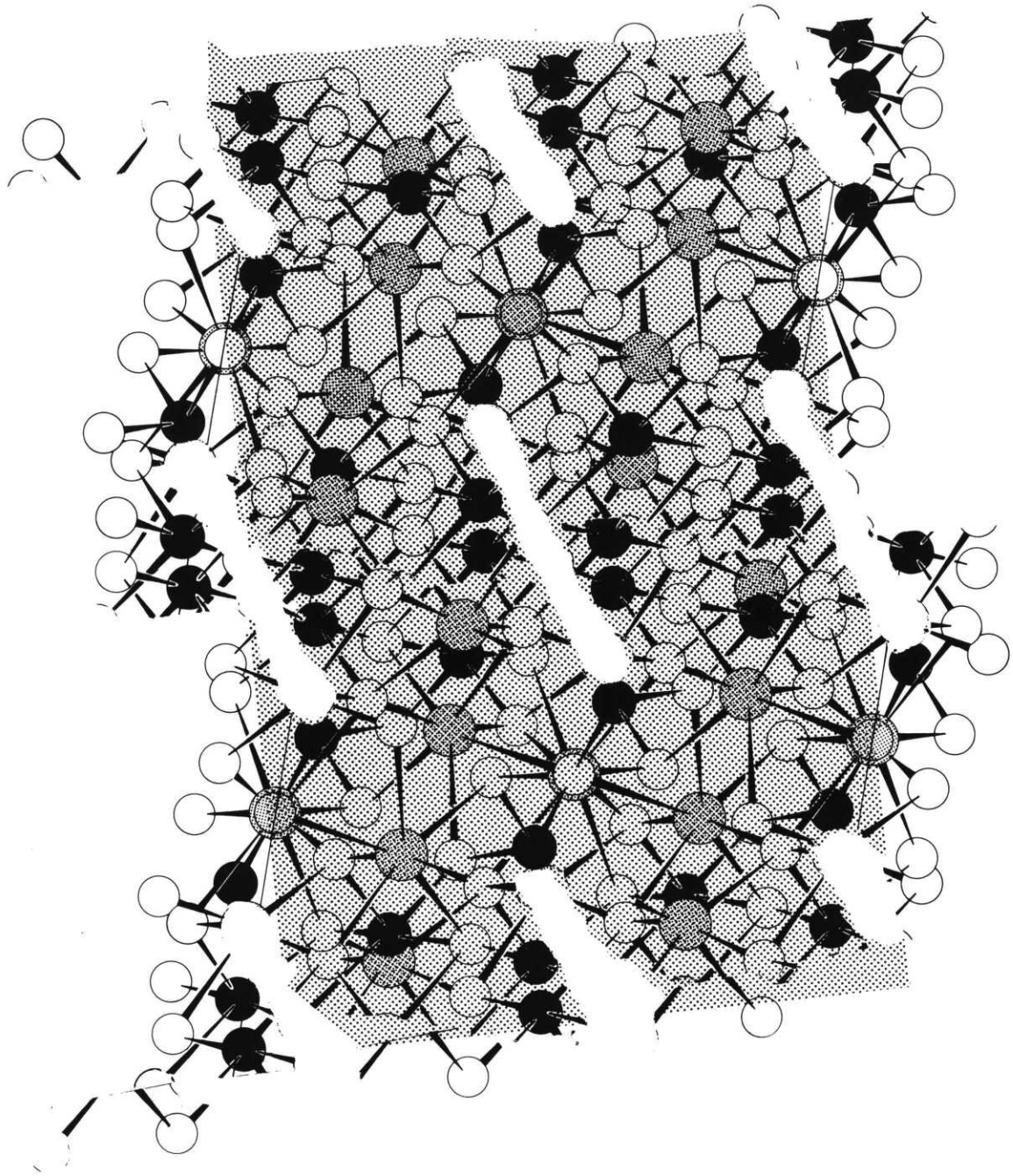
FIGURE 17
"Making" Fuloppite from Plagionite
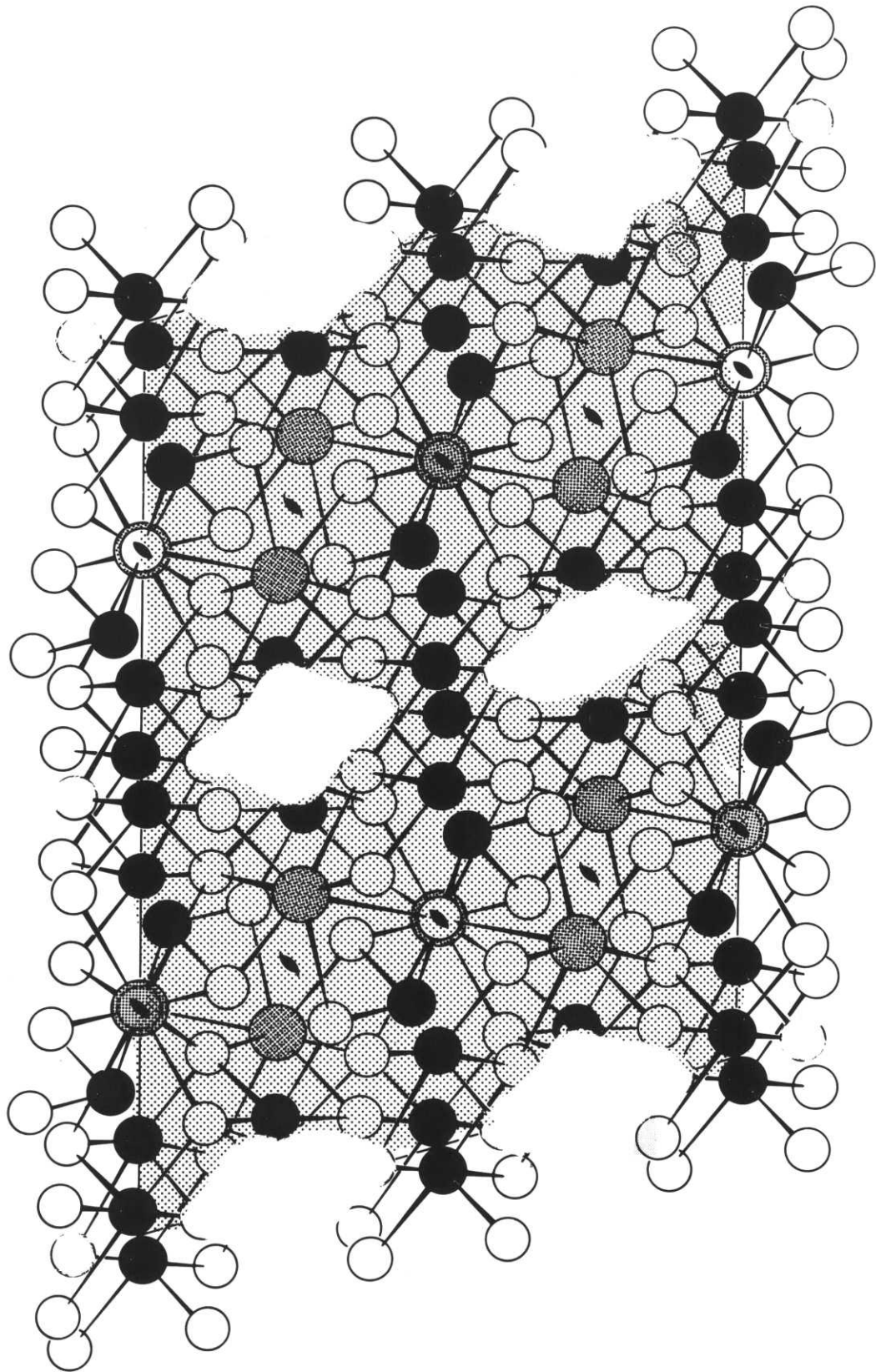
FIGURE 18
Predicted (010) Projection-Fuloppite
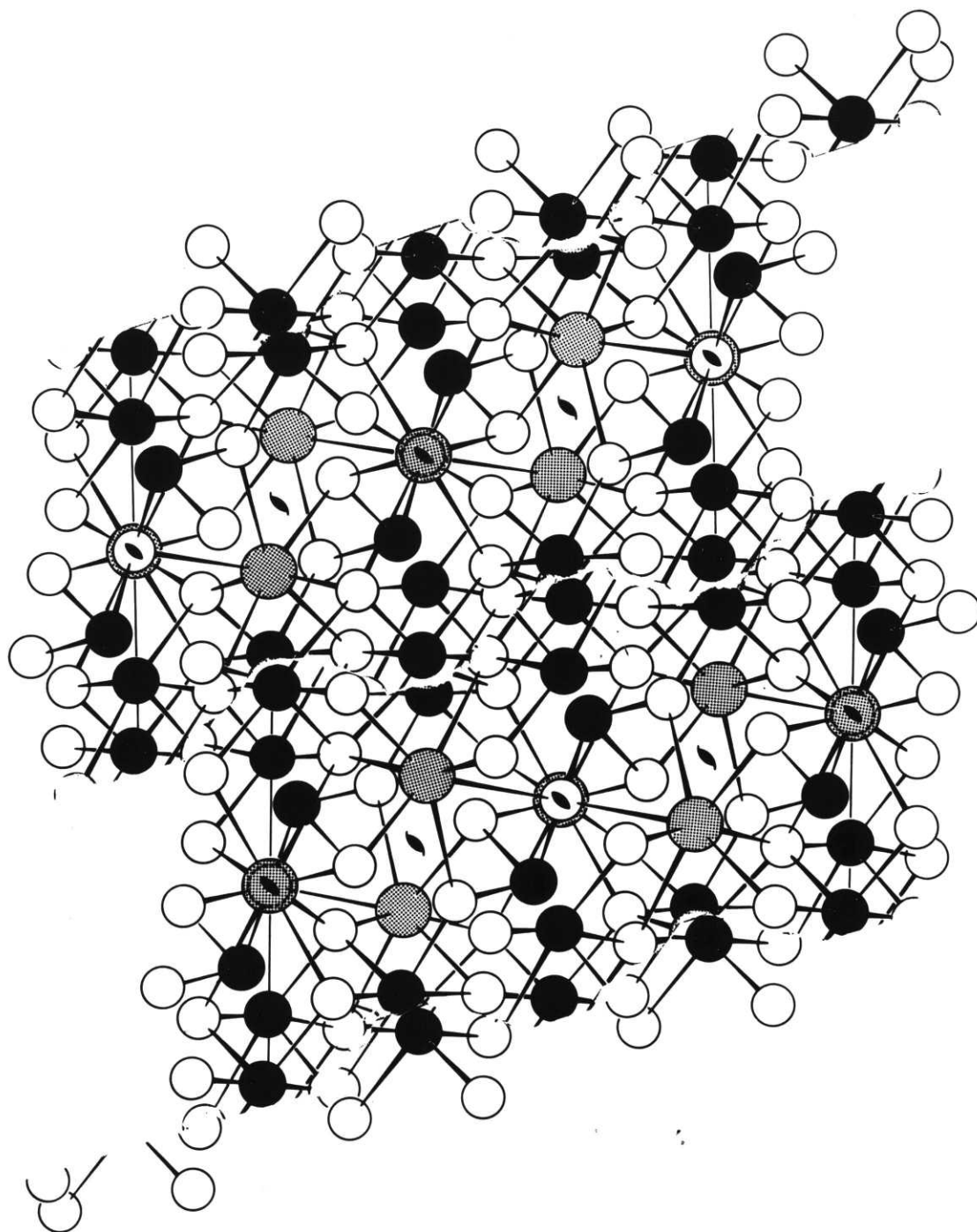
FIGURE 19

Schematic (112) Projections for the Plagionite Group

Fuloppite

Pb^2 s   Sb   S
S   Pb   S   Sb   S
     S   Sb   S   Sb S^2

Heteromorphite

Pb^2 S   Pb   S   Sb   S
S   Pb   S   Sb   S   Sb S^2
     S   Pb   S   Sb   S

Plagionite

Pb^2 S   Pb   S   Sb S^2
S   Pb   S   Sb   S
     S   Sb   S   Sb   S

Semseyite

     S   Sb   S   Pb   S Pb^2
S^2 Sb   S   Pb   S   Pb   S
     S   Sb   S   Sb   S   Pb   S
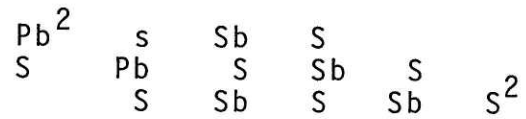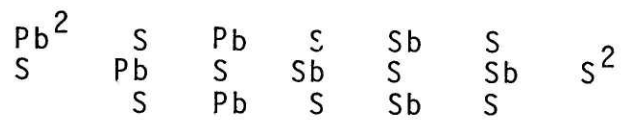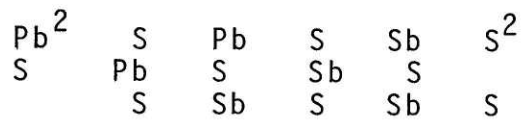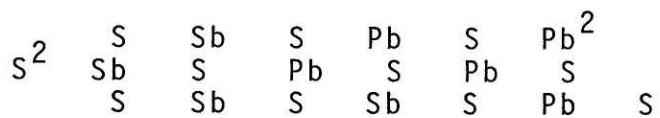
Superscript 2 denotes atom located in 2-fold position

addition process (Figure 11). This should yield a cell with $\beta \sim 90°$, $c \sin\beta \sim 25.8$ A°, $a=a_s$, $b=b_s$. This process is shown in Figure 20. It would also appear that an additional PbS could be added, the second addition process, to form para-semseyite. There seems to be no reason why this process can not be repeated again and again, leaving the Pb(1) and Sb(4) region undisturbed with alternating type 1 and type 2 additions. Although these additional compounds are not known to be naturally occuring, their appearance may be hindered only by kinetics in nature and they perhaps may be synthetically prepared.

Thus the plagionite group is indeed a homologous series. It might be better expressed as $2nPbS[PbSb_8S_{13}]$ with n=1 fülöppite, n=2 plagionite, n=3 heteromorphite, n=4 semseyite... The space group C 2/c characterizes the series and a and b remain relatively invariant as $c \sin\beta$ increases with n. The odd-numbered compounds (n=1,3,5,...) have the fülöppite structure with $\beta \sim 90°$. The even-numbered ones (n=2,4,6...) have the plagionite configuration with $\beta \sim 107°$.

The basis of the homology is the addition of PbS to the interior, not the edge, of the rock-salt like slab. The region at the edges of the slab remains invariant throughout the series. There are two types of addition - 1) the fülöppite-plagionite addition, and 2) the plagionite-heteromorphite addition. The linear increase of $c \sin\beta$, β, and the increase in density as n increases are all predicted by these models.

FIGURE 20   105
"Making" Para-Heteromorphite from Semseyite
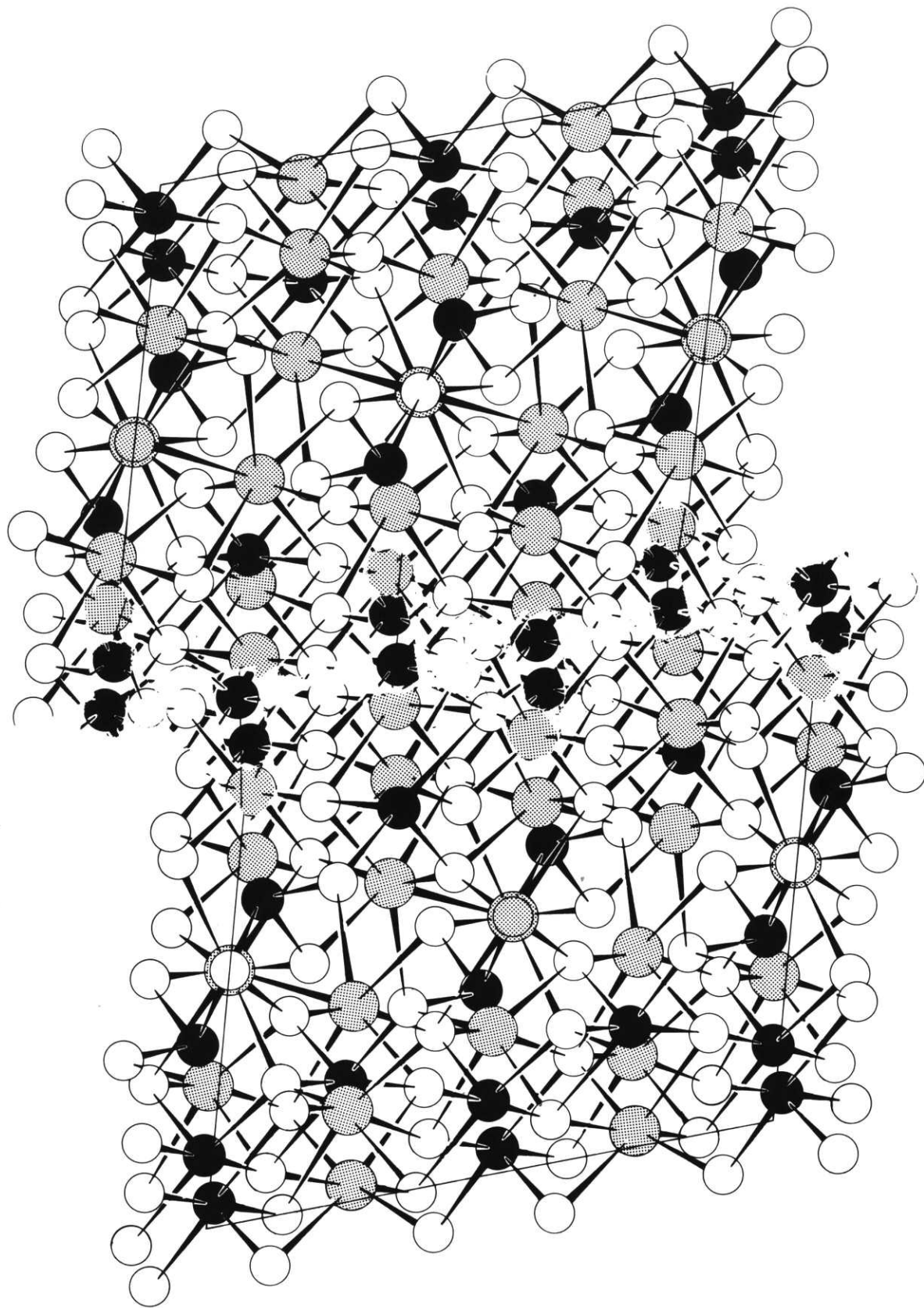
Appendix A

Film Methods versus Counter Techniques

In the course of this work two methods were used to acquire two data sets, both of which were subsequently used for structure determination and refinement. The first method involved recording the reflection intensities on film and then scanning the film with a photodensitometer. The second method utilized an automated four-circle diffractometer with monochromated radiation.

With the film technique, all the data from one hkℓ level was recorded simultaneously. A pack of three films was used for each level so that the intensity of both the strongest and weakest reflections might be recorded within the linear region of the film's recording range. The stability of the x-ray intensity within one level was not a problem as it would be if the data were recorded sequentially. The whole process to record eight levels took nearly seven weeks - a time comparable with that required to collect the data with a manual diffractometer. It must be confessed that the film method required far less effort on the experimenter's part than a manual diffractometer method would have. In addition the problem of the counter stability was eliminated and that of generator stability minimized.

On the other hand the collection of an equivalent data set with a computer-controlled automated four-circle diffractometer was even more efficient. To collect some 2200 intensities only

four days were required. The problems of generator and counter
stability although present were reduced by the rapid collection
process. The main drawback of such a process is that - while
every laboratory has the equipment to record film data - many
laboratories do not possess such expensive instrumentation as the
automated four-circle diffractometer.

The advantages of the diffractometer data become immediately
evident when data reduction begins. With the second method one
is presented for each hkℓ reflection a peak intensity, background
counts on either side of the peak, a background counting time and
a peak counting time. This data may be easily manipulated to pro-
vide an integrated intensity plus a standard deviation well docu-
mented by counting statistics. With film methods, the experimenter
is faced with a stack of films whose photodensity he must evaluate.
There are basically three approachs:

    a)   the strong, medium, weak visual estimations,

    b)   manual scanning and strip chart recording of densities,

or c)   scanning with an autophotodensitometer and receiving a
digitized density. The first alternative is not consistent in
accuracy with that of the rest of the structure determination
procedure. The second is painstaking and tedious but possible;
although stability questions arise about the light source. The
last of the three is, at least theoretically, the most accurate
and efficient. Even with this alternative the experimenter is
left with a digitized record of his film which still must be in
dexed and then integrated. Various techniques can be employed to

interpret the film. If the locations of two points on the film are known, the digital record may be indexed and with suitable computer programs a "window" around each hkℓ reflection may be examined, the peak integrated and a background correction made. This method requires great faith in (1) the exact orientation of the film relative to the scanner (i.e. the film's horizontal axis must exactly correspond with the scanner's horizontal travel) and (2) the ability of the computer program to separate peak from background and not to include an adjacent peak in the computation. Instead of trusting the computer program to be so discriminating one could just request that each hkℓ window be 'dumped', allowing him to integrate manually each reflection. Still the computer has indexed the film so that the orientation must still be exact. This is an especially critical assumption is reflections are closely spaced - as will happen with cell dimensions as small as 20 A°. The last resort is to reconstruct the film by merely 'dumping' the complete digitized record of the film just as it was recorded. Then the output can be graphically indexed much as a regular film would be. This alternative presents two problems. Indexing can be a non-trivial matter with moderately large or large lattice constants when Weissenberg films are used. Secondly the amount of output generated is giantic. For the top half of a Weissenberg film with Cu Kα radiation, the reconstructed 'film' will be nearly five feet high and eighteen feet long - all covered with numbers. The reflections, once indexed, can be manually integrated.

Thus it can be easily seen that the diffractometer yields intensities more rapidly, with less tedium and for far less cost than film methods can. To process 2000 reflections to get integrated intensities would cost a mere $10 - $20 (at the MIT computation center) for diffractometer data but nearly $1000 for film data. The time involved for diffractometer data is that needed to punch the computer cards while film data requires a minimum of several exhaustive days per level (depending on the number of reflections). The accuracy of the diffractometer is well determined by counting statistics but that of film data has yet to be determined on any mathematical basis. As final proof of the 'goodness' of the diffractometer data, the final R values of the film data and the diffractometer data are submitted: R_{film} = 18.9% (plus misplaced and missing sulfurs) while $R_{diff.}$ = 10.0% - a correct structure.

In complete fairness this test of the film technique was particularly severe. With a small weakly-diffracting crystal and utilization of the Weissenberg camera without monochromated radiation, all the disadvantages of the film methods are amplified. If the precession camera could have been used, data reduction would have been somewhat simplified. Thus until improved methods of evaluation of the photodensity are found - the diffractometer method (with good electronics) must be said to be superior to the film method and the equipment employed in this study when used in these sulfosalt structure determinations.

Appendix B

The Concept of the Direct Method

One of the basic problems of the crystallographer is determining the phase factor of the structure factor. The structure factor, $F_{hk\ell}$, is

$$F_{hk\ell} = \sum_{j=1}^{N} f_j \, e^{2\pi i(hx_j+ky_j+\ell z_j)} \tag{1}$$

where there are N atoms in the unit cell with scattering factors f_j and atomic coordinates $x_j y_j z_j$. Only the intensity (proportional to $|F|^2$) can be measured. While the Patterson method extracts interatomic distance information from $|F|^2$, the direct methods are a means of getting information about phases from $|F|$'s.

Harker and Kasper (1948) initially found several relationships among the structure factors. One can apply the Cauchy Inequality:

$$\left| \sum_{i=1}^{N} a_i b_i \right|^2 < \left(\sum_{i=1}^{N} |a_i|^2 \right)\left(\sum_{i=1}^{N} |b_i|^2 \right)$$

to the structure factor relationship (1) yielding:

$$|F_{hk\ell}|^2 < \sum_{j=1}^{N} (\sqrt{f_j})^2 \sum_{j=1}^{N} (\sqrt{f_j} \, e^{2\pi i(hx_h+ky_j+\ell z_j)})^2 .$$

This is more simply:

$$|F_{hk\ell}|^2 < \left(\sum_{j=1}^{N} f_j \right)^2 = F_{000}^2 \quad .$$

Defining the unitary structure factor as

$$U_{hk\ell} = F_{hk\ell} / \sum_{j=1}^{N} f_j \qquad (2)$$

one then obtains the fundamental inequality relationship

$$|U_{hk\ell}|^2 < 1. \qquad (3)$$

All this work presupposes only symmetry 1. Now if an inversion center is considered at the origin,

$$F_{hk\ell}^2 < F_{000} [\ 0.5\ F_{000} + 0.5\ F_{2h\ 2k\ 2\ell}\ ] .$$

Recalling that $F_{000} = \sum_i f_i$ and using the unitary structure factor yields:

$$U_{hk\ell}^2 < 0.5(\ 1 \pm |U_{2h2k2\ell}|\ ) . \qquad (4)$$

If the magnitude of $U_{hk\ell}$ and $U_{2h2k2\ell}$ are sufficiently large, then the sign of $U_{2h2k2\ell}$ must be positive. A study of some examples presented in Table 1 reveals the importance of relationship (4). With the consideration of additional symmetry, more relationships similar to (3) and (4) can provide further clues to the phase factors.

As is apparent in Table 1 only in a small number of cases is it possible to predict with certainty the sign of $U_{hk\ell}$. However Sayre (1952) lead the development of a means of probabilistically determining the phase factor. He showed that

$$F_{hk\ell} = \phi_{hk\ell} \sum_{h'} \sum_{k'} \sum_{\ell'} F_{h'k'\ell'} F_{h-h'k-k'\ell-\ell'} \qquad (5)$$

with $\phi_{hk\ell}$ being a scaling term. The implication is that the sign of $F_{hk\ell}$ can be calculated from a set of other known structure factors. Practically, however, it is simply impossible

TABLE 1

Phase Determination By An Inequality

$U^2_{hk\ell}$	$\lvert U_{2h,2k,2\ell} \rvert$	Phase +	Phase −	Comment
0.60	0.20	0.60	0.40	u(2h,2k,2) must be +
0.50	0.10	0.55	0.45	Must be +
0.40	0.10	0.55	0.45	Could be either
0.40	0.30	0.65	0.35	Must be +
0.25	0.50	0.75	0.25	Almost certainly +
0.25	0.30	0.65	0.35	Could be either

(after Stout & Jensen, 1968)

to know a large enough number of $F_{h-h'k-k'\ell-\ell'}$ signs to ob-
tain the sign of $F_{hk\ell}$. Sayre also demonstrated that when the
magnitude of $F_{hk\ell}$ is large and the structure centrosymmetric,
the series tended strongly in one direction (i.e. + or -). This
direction he proposed is determined by

$$\mathcal{S}(F_{hk\ell}) \sim \mathcal{S}(F_{h'k'\ell'}) \cdot \mathcal{S}(F_{h-h'k-k'\ell-\ell'}) \qquad (6)$$

where $\mathcal{S}$ means sign of. Hauptmann and Karle (1953) proposed for
centrosymmetric space groups, the phase relations were better
given as

$$\mathcal{S}(F_{hk\ell}) \sim \Sigma \quad \mathcal{S}(F_{h'k'\ell'}) \cdot \mathcal{S}(F_{h-h'k-k'\ell-\ell'}) \qquad (7)$$

which resembles the basic relation (5). They also showed that
the probability that equation (7) was true is given as

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (8)$$

$$P_{\pm}(E_{hk\ell}) = 0.5 + 0.5 \tanh[\frac{\sigma_3}{\sigma_2^3/^2} \, |E_{hk\ell}| \, \Sigma_{h'k'\ell'} E_{h'k'\ell'} E_{h-h'k-k'\ell-\ell'}]$$

where $\sigma_n = \sum\limits_{j=1}^{n} n_j^n$ and $n_i = f_i / \sum\limits_{j=1}^{N} f_j$ and $E_{hk\ell}^2 = U_{hk\ell}^2 / \overline{U}^2$.

$\overline{U}^2$, the average of all unitary structure factors including syste-
matically absent reflections (if any) is expressed by

$$\overline{U}^2 = \sum\limits_{i=1}^{N} n_i^2 \quad .$$

It should be remembered that F's, U's, and E's all have the same
sign or phase although they possess different magnitudes. For
the U's and E's each atom is assumed to be a point in the struc-
ture factor calculation. Applying these relationships yields

$$E^2_{hk\ell} = |F_{hk\ell}|^2 / \varepsilon\Sigma f^2_i$$

where ε is an integer which equalizes the importance of $E_{hk\ell}$'s and is dependent on the space group. For general reflections ε is 1 but in classes where systematic extinctions occur it is greater than unity.

In practice crystallographers use these relations probabilistically in a process called Symbolic Addition (SAP). The essence of the procedure is to assign literal (A,B,C,) signs to several reflections with $E_{hk\ell}$'s greater than some large value (like 2.0). Then further signs can be assigned by relation (7) with probability of being correct calculated by equation (8). The choice of starting $hk\ell$ reflections can not be arbitrary. The following criteria must be applied:

1) the magnitude of E must be large,

2) the reflections must have many interactions with the rest of the data set - e.g. if all even $hk\ell$'s are chosen then only reflections with $hk\ell$ even will be signed. Contradictions may occur after several cycles of symbolic addition, e.g. E_{451} may be assigned + in an earlier cycle but later be signed - . Therefore conditions must be established for the accep⁻ of the sign. These usually involve:

1) the minimum accep   probability for sign correctness,

2) the minimum number of affirmative contributions to each individual sign,

3) the maximum number of inconsistencies acceptable, and

4) the minimum ratio of contributors to inconsistencies.
At the conclusion of the iterations the contra. . . . .
are calculated for all sign combinations in which positive or
negative signs are assigned to the literal (ABC) ones. The
sign conbination with the smallest index is selected for the
assignment of $E_{hk\ell}$.

In current practice the program FAME(Dewar and Stone) takes
an arbitrarily scaled data set and converts it to normalized
structure factors. This is done by making a Wilson plot to
determine a scale factor and overall temperature factor. Sub-
sequently it calculates the statistical distribution of E_{hkl}'s
and makes a comparison with theoretical values for both centric
and acentric models. Lastly the whole list of $E_{hk\ell}$'s is examined
to determine a specific number of $E_{hk\ell}$'s to initialize Symbolic
Addition. These reflections are selected on the basis of the
conditions discussed previously.

MAGIC, a program also written by Dewar and Stone, performs
SAP for centric space groups. The $E_{hk\ell}$'s selected by FAME
initialize MAGIC with arbitrary literal signs and through iter-
ative cycles the signs of the remaining $E_{hk\ell}$'s are determined
using symbols and signs previously determined. All the contra-
dictions are summed as

$$\Sigma \quad 1/((1 + PARAM - P)(ITER.NO.))$$

where PARAM is a damping factor usually of the order of 10^{-6},
P is the probability of the sign to be true, and ITER.NO. is

the number of the iterative cycle where the contradiction occurs.
Therefore, sign contradictions with high probability occuring in
earlier cycles have greater weight than later ones.

When it is determined that more cycles will not generate
appreciable numbers of new signs, SAP is discontinued. An initial
structure can be determined with the aid of an E-map (an electron
density synthesis with E's not F's). The remaining unsigned
reflections can now be signed with the knowledge of the atomic
positions.

Appendix C

The Program - INTEN

The following is a listi ng of the computer program INTEN written for the IBM 370 in Fortran 4. This program enables the digitized densities of the Weissenberg film to be convert- ed into intensities.

```
C       MAIN PROGRAM
        REAL*4 TITLE(20),WAVE(2)
        INTEGER*2 IXC(2),IYC(2)
        INTEGER*2 IH(3,1600),IXX1(1600),IXX2(1600),IYY1(1600),IYY2(1600)
        COMMON/BLKA/XLIM,YLIM,RS,LREC,NREC,IXC,IYC
        COMMON/BLKB/ UR,CR,XR,YR,C1,C2,ISET,KOUNT,IDX,IDY
        COMMON/BLKC/A,B,C,AL,BE,GA,WAVE,EQUI
        COMMON/BLKD/OMS,OML,J,UPS,OM,HH,HK,HL,ICHK,STH,L,CEQS
        COMMON/BLKE/IDT,IST1,ITEMP
        COMMON/BLKX/TK2,TL2,OMD
        COMMON/BLKL/IH,IXX1,IXX2,IYY1,IYY2
        READ (5,899) NFILM
899     FORMAT (I2)
        NLOOP=0
  1     READ (5,901) TITLE
901     FORMAT (20A4)
        WRITE (6,900) TITLE
900     FORMAT (1H,20A4)
        READ(5,905) IDT,IST1,ITEMP,IDX,IDY,ISHORT,XLIM,YLIM,RS
905     FORMAT(6I3,3F5.0)
        LREC = XLIM/RS
        NREC = YLIM/RS
        WRITE (6,990) XLIM,YLIM,RS,LREC,NREC
990     FORMAT(1H0,'DENSITOMETER CONSTANTS'/10X,'XLIM = ',F7.2,' MM.'/
       1 10X,'YLIM = ',F7.2,' MM.'/10X,'RASTER SIZE = ',F5.2,' MM.'/10X,
       2 'LENGTH OF RECORD = ',I5,/10X,'NUMBER OF RECORDS = ', I5)
30      READ (5,920) A,B,C,AL,BE,GA,WAVE(1),WAVE(2),EQUI
        WRITE (6,940) A,AL,B,BE,C,GA
        WRITE (6,945) WAVE(1),WAVE(2),EQUI
        IDX2 = IDX * 2
        IDY2 = IDY *2
        WRITE (6,946) IDX2,IDY2
        IF (ISHORT) 35,40,35
35      LREC = (LREC/2) - 4
        READ (5,995) IXC(1),IYC(1),IXC(2),IYC(2)
        GO TO 50
```

```
40      CALL REFLOC(IERR)
        GO TO 897
        IF(IERR) 898,50,898
50       CALL CAMCON
        IKL=4
        CALL SET(IKL)
        WRITE(6,1020)KOUNT
        WRITE(6,950)
        CALL SORT
897     CONTINUE
        CALL INTEN
        REWIND IST1
898      NLOOP = NLOOP + 1
        IF(NLOOP - NFILM) 1,1000,1000
1000    REWIND IDT
945     FORMAT(' WAVELENGTH OF RADIATION USED'/10X,'ALPHA(1) = ',F8.6,
     1 2X,'ANGSTROMS'/10X,'ALPHA(2) = ',F8.6,2X,'ANGSTROMS'/'EQUIINCLINA
     2TION ANGLE = ',F10.6,2X,'DEGREES')
1020    FORMAT( ' KOUNT = ',I6)
995     FORMAT(4I5)
920     FORMAT(9F8.6)
940     FORMAT(' RECIPROCAL CELL DIMENSIONS'/10X,'A* = ',F10.6,2X,
     1 'ALPHA* = ',F10.6/10X,'B* = ',F10.6,3X,'BETA* = ',F10.6/10X,
     2 'C* = ',F10.6,2X,'GAMMA* = ',F10.6/)
950     FORMAT(' END OF PART ONE')
946     FORMAT(' SIZE OF LARGEST REFLECTION ON FILM',/10X,'X = ',I6,/,
     1 10X,'Y = ',I6)
        STOP
        END
C       SUBROUTINE INTEN
C       THIS IS THE PART THAT READS THE DENSITY DATA AND ORGANIZES IT.
        SUBROUTINE INTEN
C        INTEN SUBROUTINE
        INTEGER*2 LDEN(776,50),RECNUM,IXC(2),IYC(2)
        INTEGER*2 IY1,IY2,IUF
        INTEGER*2 IH,IK,IL,IX1,IX2,NY1,NY2
        REAL*8 OD(194,60)
        COMMON/BLKB/ UR,OR,XR,YR,C1,C2,ISET,KOUNT,IDX,IDY
        COMMON/BLKA/XLIM,YLIM,RS,LREC,NREC,IXC,IYC
        COMMON/BLKE/IDT,IST1,ITEMP
        COMMON/LIST/IH,IK,IL,IX1,IX2,NY1,NY2,IY1,IY2,IUF
        COMMON/BLKY/LDEN
        EQUIVALENCE(OD(1,1),LDEN(1,1))
C       THE VALUE OF IEND1 IS DETERMINED BU THE LDEN(1550,IEND1) DIMENSION
        IEND1=50
        ID=0
        IO = 0
        I1=0
        I2=0
        I3=0
3        LR2=LREC/2
        MT = LR2 * 2
        IF(LREC-MT) 102,103,102
102       LR2= LR2 + 1
```

```
1C3      LREC = LR2
         NR2= NREC/2
         MT= NR2*2
         IF(NREC-MT) 321,3201,321
321      NREC = MT + 1
         GO TO 3202
3201     NREC= MT
3202     CCNTINUE
         DO 5 I=1,IEND1
5        READ(ITEMP)(OD(J,I),J=1,194)
         IYBEG = C
         LERR= 0
         DO 130 NINT=1,22
         ICHK = 0
         READ (IST1) IH,IK,IL,IX1,NY1,IX2,NY2
323      FORMAT(3I3,2X,4I4)
C        TEST IF REFLECTION TOO CLOSE TO EDGE
C         TEXT X DIRECTION
         IF(IX1-IDX) 120,120,10
10         IF((LREC-IX2)-IDX) 120,120,20
20       IY1 = NY1-IYBEG
         IY2=NY2-IYBEG
22       IF(IY1-8) 120,120,30
30        IF(IEND1-(IY2 + 12)) 40,60,60
40        IF(LERR) 120,50,12C
C        UPCATE LDEN MATRIX
5C         INC = IY1-IO
         ISTOP = IEND1 - INC
C        DOES NEXT REFLECTION APPEAR AT A GREATER DISTANCE THAN IDEN1
         IF (ISTOP) 502,502,504
502       DO 503 J=1,IEND1
503         READ(ITEMP,END=320) (OD(I,J),I=1,194)
         IYBEG = IYBEG + IEND1
         IY1= IY1 -IEND1
         IY2= IY2-IEND1
         GO TO 22
C     ELIMINATE USED PCRTICN OF LDEN MATRIX
504      DO 3C5 I =1,ISTCP
         II = I + INC
         DO 305 J = 1,LREC
305      LDEN(J,I)=LDEN(J,II)
C        READ IN NEW VALUES TO REPRACE THOSE DISCARDED
         DO 310 J=1,INC
         JJ = ISTCP + J
310      READ(ITEMP,END=320)(OD(I,JJ),I=1,194)
         GO TO 55
320       IEND2=J-1
         LERR= -1
55        IYBEG = IYBEG + INC
         IY1=IY1-INC
         IY2=IY2-INC
60        INTSUM =0
         IERR=C
         CALL CISPLA
```

```
120       CONTINUE
130         CONTINUE
          RETURN
          END
C         SUBROUNTIEN REFLOC
          SUBROUTINE REFLOC(IERR)
C         REFLOC SUBROUTINE
            INTEGER *2 RECNUM
          LOGICAL*1 OA(1552),CB(3104)
          REAL*8OP(194),LIST(194)
          INTEGER*2LDEN(1552),LCDEN(776),IY(50),IX(50),IXC(2),IYC(2)
          INTEGER*4 IXMAX(50),IXMIN(50)
            EQUIVALENCE(OA(1),OP(1))
          COMMON/BLKA/XLIM,YLIM,RS,LREC,NREC,IXC,IYC
          COMMON/BLKE/IDT,IST1,ITEMP
           EQUIVALENCE(LDEN(1),OB(1))
          EQUIVALENCE(LCDEN(1),LIST(1))
          IERR = 0
          DO 10 J=1,1552
10        LDEN(J)=0
          NREC = 0
          MM=C
          M=0
          LREC = LREC-4
          LR=LREC/8
          LR8= LR*8
          DO 19 I=1,776
19        LCDEN(I)=0
          NRC = 0
20        READ (IDT,920,END=70) RECNUM,(OP(J),J=1,LR)
          NREC=NREC+1
          DO 30 J=1,LR8
          JJ=J+J
30        OB(JJ)= CA(J)
          DO 50 I=1,LR8
          IF(LDEN(I)) 50,40,50
40        M = M + 1
          IX(M)= I
50        CONTINUE
          NRC=NRC + 1
          IKK = 1
          DO 501 KK = 1,LR8,2
          LCP=LDEN(KK) + LDEN(KK+1)
          LCDEN(IKK)= LCP + LCDEN(IKK)
          IKK = IKK + 1
501        CONTINUE
          IF(NRC-2) 503,502,5C4
503       GO TC 5C31
504         WRITE(6,5041)
5C41      FORMAT(' CALLING EXITE ERROR IN COMPACTION PROCESS')
          CALL EXIT
502       WRITE (ITEMP) LIST
          NRC = 0
          DO 5021 JK=1,IKK
```

```
5021      LCDEN(JK)=0
5031       CONTINUE
          IF(M) 60,20,60
60        MM=MM+1
          IXMAX(MM)= IX(M)
          IXMIN(MM)=IX(1)
          IY(MM) = NREC
          M=0
          GO TO 20
70        WRITE (6,970)        NREC
210       CONTINUE
          END FILE ITEMP
          REWIND ITEMP
           GO TO 999
          WRITE (6,930)
          DO 220 JJ=1,MM
220       WRITE(6,940)IY(JJ),IXMIN(JJ),IXMAX(JJ)
          KK=0
          L=0
230       MIN=5000
          MAX=0
          KY=0
240       L = L+ 1
          IF (IY(L)-(IY(L+1)-1)) 270,250,270
250       MAX = MAXO(IXMAX(L),MAX)
          MIN = MINO(IXMIN(L),MIN)
          KY = KY + 1
          IF (L+1-MM) 240,260,260
260       L = L+ 1
270       BMAX= AMAXO(IXMAX(L),MAX)
          BMIN=AMINO(IXMIN(L),MIN)
          KY=KY+1
          KK = KK +1
          IF(BMAX-BMIN) 290,280,290
280       IXC(KK)=BMAX
          GO TO 300
290       IXC(KK) = BMIN + ((BMAX-BMIN) + 0.5)/2.0
300       MID = L-(KY-2)
          IYC(KK)= IY(MID)
          IF(L-MM) 230,310,310
310       IF(KK-2) 320,330,320
320       WRITE (6,950) KK
          IERR = 1
          GO TO 1000
330       WRITE (6,960)
          WRITE(6,965)(IXC(J),IYC(J),J=1,KK)
999        CONTINUE
           LREC = LR8
          GO TO 1000
1000      RETURN
920        FORMAT(A2,2X,200A8)
940       FORMAT(1X,I6,3X,I6,3X,I6)
930       FORMAT(' RECNUM',5X,'XMIN',5X,'XMAX')
950       FORMAT(' CALLING EXIT',I6,2X,'CENTERS FOUND')
960       FORMAT('CENTERS OF REFERENCE REFLECTIONS AT'/10X,'X',10X,'Y')
```

```
             FORMAT( CENTERS OF REFERENCE REFLECTIONS
  965       FORMAT(2(5X,I6))
  970       FORMAT(' END OF FILE ON IDT, NREC CHANGED TO ',I6)
            END
  C         SUBROUTINE CAMCON   CALCULATES CAMERA CONSTATNS
  C          CAMCON SUBROUTINE
             SUBROUTINE CAMCON
            REAL*4 RIX(2),RIY(2),O(2),U(2),X(2),Y(2)
            INTEGER*2 IXC(2),IYC(2),IUPS(2)
            COMMON/BLKA/XLIM,YLIM,RS,LREC,NREC,IXC,IYC
            COMMON/BLKB/ UR,OR,XR,YR,C1,C2,ISET,KOUNT,IDX,IDY
            COMMON/BLKE/IDT,IST1,ITEMP
            C1C=2.0
            C2C =   2.0
            IKL=1
            CALL SET(IKL)
            READ(5,900) IUPS(1),IUPS(2)
            WRITE (6,899)
            DO 10 I=1,2
            RIX(I)=IXC(I)
  10         RIY(I)=IYC(I)
            IF(IXC(1)-IXC(2)) 30,20,20
  20        X(1)=RIX(1)*RS
            X(2)=RIX(2)*RS
            Y(1)=RIY(1)*RS
            Y(2)= RIY(2)*RS
            GO TO 40
  30         X(1)=RIX(2)*RS
            X(2)=RIX(1)*RS
            Y(1)=RIY(2)*RS
            Y(2)=RIY(1)*RS
  40        DO 110 J=1,2
            IF(ISET-2) 50,60,70
  50        READ(IST1) HH,HK,HL,UPS,OMEGU,OMEGL
            GO TO 80
  60        READ(IST1) HL,HH,HK,UPS,OMEGU,OMEGL
            GO TO 80
  70        READ(IST1) HK,HL,HH,UPS,OMEGU,OMEGL
  80        IF (IUPS(J)) 90,90,100
  90        O(J)=OMEGU
            U(J)=UPS
            GO TO 110
  100       O(J)=OMEGL
            U(J)= -UPS
  110        WRITE(6,905) HH,HK,HL,U(J),O(J),X(J),Y(J)
            DX=X(1)-X(2)
            DY=Y(1)-Y(2)
            DU = U(1)-U(2)
            IF (DY) 200,290,210
  200        IF (O(1)-O(2)) 220,290,230
  220        DO = O(1)-O(2)
            GO TO 300
  230       DO=(360.-O(1))+O(2)
            GO TO 300
  210       IF(O(1)-O(2)) 250,290,220
```

```
250      DU = (360. -O(2)) + O(1)
         GO TC 300
290      WRITE(6,930)
         CALL EXIT
300      C1=ABS(DU/DX)
         C2=ABS(DO/DY)
         GO TC 301
         IF(C1-(C1C+ 0.1*C1C)) 401,402,402
401       IF(C1-(C1C-0.1*C1C)) 402,402,403
403       IF(C2-(C2C+0.1*C2C))                 404,402,402
404       IF(C2-(C2C-0.1*C2C)) 402,402,301
402       WRITE(6,999)
999        FORMAT('REFERENCE REFLECTION IMPROPERLY INDEXED START AGAIN')
         WRITE(6,9991) C1,C2
9991     FORMAT (2F8.5)
         CALL EXIT
301      WRITE(6,910) C1,C2
         UR=U(1)
         OR=O(1)
         XR=X(1)
         YR=Y(1)
         WRITE (6,920) UR,OR,XR,YR
         REWIND IST1
899      FORMAT(' REFLECTIONS USED IN CALCULATING CAMERA CONSTANTS'/13X,'H'
        ',3X,'K',3X,'L',5X,'UPSILON',7X,'OMEGA',5X,'X',10X,'|')
900      FORMAT(2I1)
905      FORMAT(1CX,3F4.0/4(2X,F10.5))
910      FORMAT(' CAMERA CONSTANTS'/10X,'C1 = ',F10.5,2X,'DEGREES/MM.'/
        1 10X,'C2 = ',F10.5,2X,'DEGREES/MM.')
920      FORMAT('POSITION OF REFERENCE REFLECTION',10X,'UPSILON = ',F10.5,
        12X,'DEGREES'/10X,'OMEGA = ',F10.5,2X,'DEGREES'/10X,'X = ',
        2F10.5,2X,'MM.'/10X,'Y = ',F10.5,2X,'MM.')
930      FORMAT(' OY(2) EQUAL TO Y(1), NO SOLUTION FOR C2***CALLING EXIT')
         RETURN
         END
C        SUBROUTINE SET /SETS UP HLKS IN PROPER ORDER TO BE READ
         SUBROUTINE SET(IKL)
C        SET SUBROUTINE
         INTEGER*2 IXC(2),IYC(2)
         REAL*4 WAVE(2),WSQ(2),AXIS(3),UPS(2),OMEGU(2)
         COMMON/BLKA/XLIM,YLIM,RS,LREC,NREC,IXC,IYC
         COMMCN/BLKB/ UR,OR,XR,YR,C1,C2,ISET,KCUNT,IDX,IDY
         CCMMON/BLKC/A,B,C,AL,BE,GA,WAVE,EQUI
         COMMCN/BLKD/OMS,OML,J,UPS,OM,HH,HK,HL,ICHK,STH,L,CEQS
         COMMCN/BLKE/IDT,IST1,ITEMP
         COMMON/BLKX/TK2,TL2,OMD
         DATA AXIS/'C ','B ','A '/
         KOUNT = C
         JMP=1
         IF (IKL-4) 40,10,40
C        CALCULATE STARTING AND ENDING VALUES OF CMEGA
10       OMS= OR-(YR*C2)
         IF (CMS) 20,30,30
20       OMS = OMS + 360.0
30       OML=CMS + YLIM*C2
```

```
32        IF(CML-360.0) 36,36,34
34        OML = OML-360.0
          GO TC 32
36        WRITE (6,2010) CMS, OML
          OMD=YLIM*C2
          GO TC 500
40        IF (IKL-2) 60,50,60
50        IKL=1
          GO TO 250
60        READ(5,1000) STHN,ISET,MH2,MK2,ML2
1000      FCRMAT(F10.5,4I3)
          WRITE(6,1020) AXIS(ISET), STHN
          PI=3.14159
          PIH= PI/2.0
          RAD = PI/180.0
          WSQ(1)= WAVE(1)*WAVE(1)
          WSQ(2)=WAVE(2)*WAVE(2)
          EQUI = EQUI * RAD
          SEQ= SIN(EQUI)
          CEQ = COS(EQUI)
          LEQS=CEQ*CEQ
          IF (ISET-2) 201,202,203
C         CRYSTAL MOUNTED CN C AXIS
2C1       AP = A
          BP=B
          CP=C
          ALP = AL * RAD
          BEP = BE * RAD
          GAP = GA*RAD
          GO TO 204
C         CRYSTAL MOUNTED ALCNG B AXIS
2C2       AP = C
          BP = A
          CP = B
          ALP = GA * RAD
          BEP = AL * RAD
          GAP = BE * RAD
          GO TC 204
C         CRYSTAL MOUNTED CN A AXIS
203       AP = B
          BP = C
          CP = A
          ALP = BE * RAD
          BEP = GA * RAD
          GAP = AL * RAD
204       A = AP
          B = BP
          C = CP
          AL = ALP
          BE = BEP
          GA = GAP
          CAL = COS(AL)
          CBE= COS(BE)
          CGA = COS(GA)
          SGA = SIN(GA)
```

```
          SGA =       SIN(GA)
          ABG= 2.0*A*B*CGA
          BCA = 2.0*B*C*CAL
          CAB = 2.0*C*A*CBE
          AA = A*A
          BB = B*B
          CC= C*C
          BCG= B*CGA
          CCB = C*CBE
          BSG= B*SGA
          DC = C*(CAL-CBE*CGA)/SGA
          R = CEQ
          ZETA = 2.0*SEQ
          ZETA2=ZETA*ZETA
          IEOF = 0
250         IF(IKL-1) 300,300,500
C      READ HKL FROM CARDS
300         READ(5,301) MH,MK,ML,IEOF
301       FORMAT(4I3)
          IF (IEOF) 904,800,904
C      GENERATE HKLS FROM EXTINCTION RULES - NOT USED
C      INSTEAD GENERATE FROM CARDS
500        GO TO 300
C      COMPUTE DIFFRACTION SETTINGS
800        IF (ISET-2) 801,802,803
801       TH=MH
          TK = MK
          TL = ML
          GO TO 804
802          TH = ML
          TK = MH
          TL = MK
          GO TO 804
803          TH = MK
          TK = ML
          TL = MH
804        TLC= TL*TL*CC
          QA= TH*TH*AA + TK*TK*BB + TLC
          QB = TH*TK*ABG
          QC = TK*TL*BCA
          QD = TH*TL*CAB
C      HKL
          Q= QA+QB+QC+QD
          STH=(WAVE(1)/2.0*SQRT(Q))
          IF (STH-STHN) 810,990,990
810          HL = TL
850        HH = TH
860        HK = TK
  870      XIX = HH*A + HK*BCG + TL*CCB
          XIY = HK* BSG + HL*CC
          IF (XIX) 890,880,890
880       IF(XIY) 884,882,884
882         PHI =PIH
          GO TO 920
884        PHI=PIH -(XIY/ABS(XIY))*PIH
```

```
         GO TO 920
890      IF (XIY) 894,892,894
892      PSI = 0.0
         GO TO 910
894      XY = ABS(XIY/XIX)
         PSI = ATAN(XY)
         IF (XIY) 900,910,910
900      PSI = -PSI
910      PHI=PI-((XIX/ABS(XIX)))*(PIH+PSI)
920      PHI = PHI/RAD
         IF (IKL-1) 924,922,924
922      CALL RTEST(PHI,HH,HK,HL,Q,WSQ(1),ZETA2,R,PI)
         GO TO 250
924      ICHK = 0
         DO 930 J=1,2
         L = J
         XI2= WSQ(J)*Q-ZETA2
         IF (XI2) 9240,9240,9241
9240     WRITE(6,1030) MH,MK,ML,I,XI2
1030     FORMAT(' THE VALUE OF XI**2 FOR REFLECTION', 3I4,' SIGN GROUP',
     1I4,' IS',F10.8/'  THIS REFLECTION WILL BE IGNORED')
         GO TO 990
9241     XI=SQRT(XI2)
         XXI=XI/(2.0*R)
         IF(XXI-1.0) 9242,990,990
9242     U = 2.0*ARSIN(XXI)
         UPS(J) = U/RAD
         OMEGU(J) = PHI+UPS(J)/2.0
         IF (ICHK) 940,926,940
926      OM=OMEGU(J)
         CALL TEST
930      CONTINUE
940      ICHK = 0
         DO 980 J = 1,2
         L = 3-J
         OMEGL = OMEGU(L) + 180.0 - UPS(L)
         UPS(L) = -UPS(L)
950      IF(OMEGL-360.0) 970,960,960
960      OMEGL = OMEGL - 360.0
         GO TO 950
970      OM = OMEGL ,
         CALL TEST
         IF (ICHK) 990,980,990
980      CONTINUE
990      CONTINUE
         GO TO 250
904      END FILE IST1
         REWIND IST1
2010     FORMAT(' OMEGA START = ',F15.8/'OMEGA LIMIT = ',F15.8)
1020     FORMAT(' CRYSTAL MOUNTED ON',A2,' AXIS'/'UPPER LIMIT OF SIN(THETA
     1) = ',F15.8)
         RETURN
         END
C        SUBROUTINE RTEST
```

```
        SUBROUTINE RTEST(PHI,HH,HK,HL,Q,WSQ,ZETA2,R,PI)
        COMMON/BLKE/IDT,IST1,ITEMP
        XI= SQRT(WSQ*Q-ZETA2)
        UPS=2.0*ARSIN(XI/(2.0*R))
        UPS = UPS* (180.C/PI)
        OMEGU = PHI + UPS/2.0
        OMEGL = OMEGU + 180.0 -UPS
10      IF (OMEGL - 360.C) 30,20,20
20       OMEGL = OMEGL - 360.0
        GO TO 10
30       WRITE (IST1) HH,HK,HL,UPS,OMEGU, OMEGL
        RETURN
        END
C       SUBROUTINE TEST
C       TEST SUBROUTINE
        SUBROUTINE TEST
        REAL*4 UPS(2),YY(3),H(3)
        INTEGER*2 IH(3,1600),IXX1(1600),IXX2(1600),IYY1(1600),IYY2(1600)
        INTEGER*2 IXC(2),IYC(2)
        COMMON/BLKA/XLIM,YLIM,RS,LREC,NREC,IXC,IYC
        COMMON/BLKB/ UR,OR,XR,YR,C1,C2,ISET,KOUNT,IDX,IDY
        COMMON/BLKD/OMS,OML,J,UPS,OM,HH,HK,HL,ICHK,STH,L,CEQS
        COMMON/BLKE/IDT,IST1,ITEMP
        COMMON/BLKL/IH,IXX1,IXX2,IYY1,IYY2
        COMMON/BLKX/TK2,TL2,OMD
        H(1) = HH
        H(2) = HK
        H(3) = HL
        UP = UPS(L)
C       CALCULATE Y
        SOM = OM-OMS
10       IF (SOM) 20,30,30
20       SCM = SOM + 360.0
        GO TO 10
C       IS Y WITHIN LIMITS
30        IF(SOM-OMD) 40,4C,90
4C        Y = SOM/C2
        IY = (Y/RS) + 0.5
C       CALCULATE X
        DU = UR-UP
        DX= DU/C1
        X = XR + DX
C       IS X WITHIN LIMITS
        IF (X) 90,50,50
50       IF(XLIM-X) 90,60,60
60       IX=(X/RS) + 0.5
        IF (J-1) 80,70,80
7C        IY1 = IY + 1 -IDY
        IX2 = IX + IDX
        IF (IY1) 95,95,85
8C        IY2 = IY + IDY
        IX1 = IX + 1 - IDX
        IF (IY2-NREC) 82,82, 100
82        KOUNT = KOUNT + 1
        XX = 0.0
```

```
C        CCMPACT COORDINATES
         MT = (IX1/2)*2
         IF(MT-IX1) 101,102,101
C        IX1 ODD
101      IX1 = (IX1 +1)/2
         GO TO 103
C        IX1 EVEN
102      IX1 = (IX1/2)
1C3      MT=(IX2/2)*2
         IF(MT-IX2)104,105,1C4
C        IX2 IS ODD
1C4      IX2=(IX2+1)/2
         GO TO 106
C        IX2 IS EVEN
105      IX2 = IX2/2
C        CHECK Y COORDINATES
1C6      MT=(IY1/2)*2
         IF(MT-IY1) 107,1C8,107
1C7      IY1=(IY1+1)/2
         GO TO 109
1C8      IY1=IY1/2
109      MT= (IY2/2)*2
         IF(MT-IY2) 110,111,110
110      IY2=(IY2+1)/2
         GO TO 112
111      IY2 = IY2/2
112      CCNTINUE
         DO 240 I=1,3
24C      IH(I,KOUNT)=H(I)
         IXX1(KOUNT) = IX1
         IXX2(KOUNT) = IX2
         IYY1(KOUNT) = IY1
         IYY2(KOUNT)=IY2
85       ICHK = C
         GO TO 100
90       IF(J-2) 95,100,95
95       ICHK=1
100      RETURN
         END

C        SUBROUTINE SORT
C        NREC NOW COMPACTED
         SUBROUTINE SORT
C        SORT SUBROUTINE
         INTEGER*2 IH(3,16CC),IXX1(1600),IXX2(1600),IYY1(1600),IYY2(1600)
         INTEGER*2 IXC(2),IYC(2)
         COMMON/BLKA/XLIM,YLIM,RS,LREC,NREC,IXC,IYC
         CUMMON/BLKB/ UR,OR,XR,YR,C1,C2,ISET,KOUNT,IDX,IDY
         COMMCN/BLKE/IDT,IST1,ITEMP
         COMMCN/BLKL/IH,IXX1,IXX2,IYY1,IYY2
         L=0
         MM=(NREC/2)*2
         IF(MM-NREC) 1,2,1
1        NREC=(NREC+1)/2
```

```
        GO TO 3
2       NREC= NREC/2
3        CONTINUE
        DO 100 J=1,NREC
        DO 100 K=1,KOUNT
        IF(IYY1(K)-J) 100,90,100
90      L = L+1
        IF (ISET-2) 10,20,30
C       CRYSTAL MOUNTED ON C AXIS
10      WRITE(IST1)(IH(JJ,K),JJ=1,3),IXX1(K),IYY1(K),IXX2(K),IYY2(K)
        GO TO 100
C       CRYSTAL ON B AXIS

20      WRITE(IST1)IH(2,K),IH(3,K),IH(1,K),IXX1(K),IYY1(K),IXX2(K),
     1 IYY2(K)
        GO TO 100
C       CRYSTAL ON A AXIS
30      WRITE(IST1)IH(3,K),IH(1,K),IH(2,K),IXX1(K),IYY1(K),IXX2(K),
     1IYY2(K)
100      CONTINUE
        END FILE IST1
        REWIND IST1
        WRITE(6,900) KOUNT, L
        KOUNT = L
        RETURN
900      FORMAT( 1H0, 20X,I6,' REFLECTIONS CALCULATED ', I6, 'REFLECTIONS
     1ERED')
        END


C       SUBROUTINE DISPLA
C       THIS SUBROUTINE DISPLAYS THE INTENSITY DATA AND THE PARTIAL SUMS
        SUBROUTINE DISPLA
C       DISPLA SUBROUTINE
        INTEGER*2 IH,IK,IL,IX1,IX2,NY1,NY2,IY1,IY2,IUF
        INTEGER*2 LDEN(776,50),RECNUM,IXC(2),IYC(2)
        REAL*8 OD(194,60)
        EQUIVALENCE (OD(1,1),LDEN(1,1))
        COMMON/BLKE/IDT,IST1,ITEMP
        COMMON/LIST/IH,IK,IL,IX1,IX2,NY1,NY2,IY1,IY2,IUF
        COMMON/BLKY/LDEN
        WRITE(6,900) IH,IK,IL
        WRITE(6,910)IX1,IX2,IY1,IY2
        IB1=0
        J1=IX1
        J2=IX2
        IBKR=IY2
        IBKL=IY1
        WRITE(6,920) NY1,NY2
        IDI=IBKR-IBKL
        IF(IDI-28) 20,20,10
10       IB2=IBKL + 28
        IB1 = IB2 +1
        GO TO 25
20       IB2=IBKR
25        DO 30 J=J1,J2
```

```
30      WRITE(6,930)(LDEN(J,I),I=IBKL,IB2)
        IF(IB1) 40,60,40
40        WRITE (6,940)
        DO 50 J =J1,J2
50      WRITE(6,930)(LDEN(J,I),I=IB1,IBKR)
60        RETURN
900      FORMAT(' DISPLAY OF REFLECTION',5X,3I4)
910      FORMAT(' COORDINATES OF REFLECTION ARE '/10X,'X',I6,'TO',I6/
        110X,'Y',I6,'TO',I6/)
920      FORMAT(' DISPLAY STARTS 4 POSITIONS ABOVE REFLECTION AND ENDS J
        1POSITIONS BELOW',10X,'DISPLAY GOES FROM',I6,'TO',I6)
930       FORMAT(1X,28I4,2X,I6)
940       FORMAT(//////)
        END
```

```
C     TAPE SET UP  CARDS FOR IBM 370
      TAPE = UNIT 9, DISK SET UP IST1 = 12, ITEMP=13
  G.FT09F001   DD  DDNAME=TAPE
  G.TAPE   DD  DSNAME=USERFILE.M6569.6541.DATA,UNIT=24009,          X
        DCB=(RECFM=U,BLKSIZE=1500,OPTCD=Z),
           VOLUME=SER=000439,DISP=(OLD,PASS),LABEL=(3,NL)
  G.FT12F001   DD  DSNAME=&&LC,UNIT=SYSDA,DISP=(NEW,DELETE),
      SPACE=(2408,(1000,9)),DCB=(RECFM=VS,BLKSIZE=2408)
  G.FT13F001   DD  DSNAME=&&LD,UNIT=SYSDA,DISP=(NEW,DELETE),        X
      SPACE=(2408,(1000,9)),DCB=(RECFM=VS,BLKSIZE=2408)
  G.SYSIN   DD *
C     INPUT DECK
1.    NUMBER OF FILMS (I2) NFILM
2.    TITLE CARD (20A4)
3.    TAPE CONTROL CARD (6I3,3F5.0)
1-3   IDT TAPE UNIT # = 9
4-6   IST1 FIRST DISK UNIT # = 12
7-9   ITEMP SECOND DISK NUMBER = 13
10-12   IDX - HALF WIDTH IN X DIRECTION OF LARGEST PEAK IN MM/RASTER
            SIZE(MM)
13-15   IDY - HALF WIDTH IN Y DIRECTION OF LARGEST PEAK
      IN MM/RASTER SIZE(MM)
16-18   ISHORT - PROCESSNG INDICATOR ALWAYS =0
19-23   XLIM - X-LENGTH SCANNED IN MM
24-28   YLIM - Y LENGTH SCANNED IN MM
29-33 RS - RASTER SIZE IN MM
4.    CELL CARD (9F8.6)
1-8   A*        A
9-16   B*        B
17-24   C*        C
25-32        *        AL
33-40 °        *        BE
41-48        *        GA
49-56          1   WAVE(1)
57-64      2   WAVE(2)
65-72            EQUI
5.    MAXIMUM LIMITS (F10.5,4I3)
1-10    SIN THETA MAX
11-13    ISET - ROTATION AXIS C=1,B=2,A=3
14-16    MAXIMUM H
17-19    MAXIMUM K
20-22    MAXIMUM L
6.    REFERENCE REFLECTIONS (4I3)
1-3    H
4-6    K
7-9    L
10.12   IEOF   =1 LAST CARD, =0 MORE FOLLOWS
      NOTE **** 3 CARDS, HKL LOWEST ON THE FILM
         (LARGEST X VALUE) INPUTED FIRST
```

```
7.    TOP BOTTOM INDICATOR
1    IUPS(1) FIRST REFERENCE REFLECTION IS ON TOP(=0)
     OR BOTTOM(=1) HALF OF FILM
2    IUPS(2)  SECOND REFERENCE REFLECTION IS ON TOP(=0)
     OR ON BOTTOM(=1) HALF OF FILM
8.    REFLECTIONS TO BE INDEXED (4I3)
1-3   H
4-6   K
7-9   L
10.12   IEOF   =1 LAST CARD, =0 MORE FOLLOWS
```
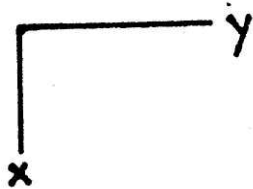
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