Short Communication

Prediction of structures in the homologous series $Pb_{3+2n}Sb_8S_{15+2n}$ (the plagionite group). By J. J. Kohatsu and

B. J. Wuensch, *Department of Metallurgy and Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139, *U.S.A.*

A subfamily of intermediate phases in the system $PbS–Sb_2S_3$ forms a monoclinic homologous series, $Pb_{3+2n}Sb_8S_{15+2n}$ ($n=0$ to 3), in which a and b remain invariant; c increases with n, and β alternates between values of *ca.* 94 and 107° in successive members. Structures have been determined for phases with $n=1$ and 3. The properties and cell geometries of remaining compounds in the series may be explained through a model which derives structures with n even by removal of a Pb–S pair from a linear asymmetric unit, shear of the structure by $\frac{1}{4}a$, and collapse along d_{001}. Undetermined structures for the remaining known phases have been predicted, and it has proved possible to extend the series to additional hypothetical members.

The system $PbS–Sb_2S_3$ contains at least 18 well defined minerals, most of which are acicular in habit and elongated along the direction of an 8 Å lattice constant. Members of the 'plagionite group' are exceptions: They lack the 8 Å periodicity and have tabular morphology. The group, Table 1, constitutes an apparent homologous series $Pb_{3+2n}Sb_8S_{15+2n}$ ($n=0$ to 3), in which a and b remain essentially invarient while c increases with n. Although β remains close to 100°, its value actually alternates between distinct values of *ca.* 94 and 107° in successive members. Jambor (1969) noted that $c\sin\beta$ increases more uniformly with n than does c. All members of the plagionite group have space group $C2/c$ and (with the possible exception of füloppite) a $\{112\}$ cleavage which increases in perfection with n.

The crystal structures of plagionite (Cho & Wuensch, 1970, 1974) and semseyite (Kohatsu, 1973; Kohatsu & Wuensch, 1974) were recently determined in this laboratory. The asymmetric units of the structures contained 4 Sb, $(n+1)$ Pb and $(n+7)$ S atoms located in the general position of space group $C2/c$, plus 1 Pb and 1 S atom each located in special position $4(e)2$. Both structures were found to consist of layers of rocksalt-like structure, two atoms in thickness, which were oriented parallel to (112) and (1$\bar{1}$2) alternately along c. The layers extended indefinitely along [$\bar{1}$10] and [110], respectively, in directions corresponding to [310] in the rocksalt structure. The asymmetric units in both plagionite and semseyite were linear chains of metal-sulfur pairs lying in (112) and extending along [110] of the rocksalt-like array.

It seems probable that the structures of successive members of the plagionite group differ only in the addition of one Pb and one S atom to a linear asymmetric unit which, in order to account for the common $\{112\}$ cleavage, must be constrained to lie in (112). Successive members would thus differ in the width of the rocksalt slab. The addition or removal of atoms, however, must account for the change in β of the cell.

It has been possible to account for the above features by (*a*) removal of one Pb–S pair from the interior of a rocksalt slab (where the coordination of all atoms is pseudo-octahedral) while leaving undisturbed a region with atoms in low and irregular coordination at the boundary between adjacent (112) and (1$\bar{1}$2) layers, followed by (*b*) slip of the structure by $\frac{1}{4}a$ and collapse of (001) to fill the void. This operation moves a Pb atom into the linear sequence of the asymmetric unit at a site previously occupied by Sb. The unknown structures of füloppite and heteromorphite have been constructed through this procedure. Projections of the proposed structures along b are presented in Fig. 1. It similarly has been possible to extend the series to additional hypothetical members by this means. Fig. 1 also presents structures predicted for hypothetical compounds with $n=4$ and 5. The projections presented for füloppite and heteromorphite are actually collages assembled from projections of plagionite and semseyite, respectively, yet the directions and lengths of the severed and reassembled bonds are remarkably undisturbed. It may be noted that the model predicts a cell of the correct dimensions for the unknown structures.

Table 1. *The plagionite group*

n	Mineral	Composition	a	b	c	β
0	Füloppite*	$Pb_3Sb_8S_{15}$	13·39 Å	11·69 Å	16·91 Å	94·68°
1	Plagionite†	$Pb_5Sb_8S_{17}$	13·4857 (8)	11·6856 (4)	19·9834 (7)	107·168 (4)
2	Heteromorphite‡	$Pb_7Sb_8S_{19}$	13·60	11·93	21·22	90·83
3	Semseyite§	$Pb_9Sb_8S_{21}$	13·603 (3)	11·935 (7)	24·452 (7)	106·046 (10)

* Nuffield (1946). † Cho & Wuensch (1970). ‡ Jambor (1969). § Kohatsu (1973).

The projections of Fig. 1 provide x and z parameters for the atoms. The y coordinates were obtained from the fact that the atoms which occupy opposite surfaces of the two-layer (112) rocksalt slab are related by an inversion center at either $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ or $\frac{1}{4}\frac{1}{4}\frac{1}{2}$, and that the thickness of the slab is known from the structures of plagionite and semseyite.

The proposed structures provide a plausible explanation for the crystallography, chemistry and properties of the plagionite group. Ideal atomic coordinates have been obtained for each of the proposed structures in Fig. 1. These will be reported in a subsequent paper, but we first intend to refine the coordinates by least-squares adjustment (Meier & Villiger, 1969) of bond lengths to the values found in plagionite and semseyite, and to test the validity of the models through comparison of experimental and computed Debye–Scherrer patterns.
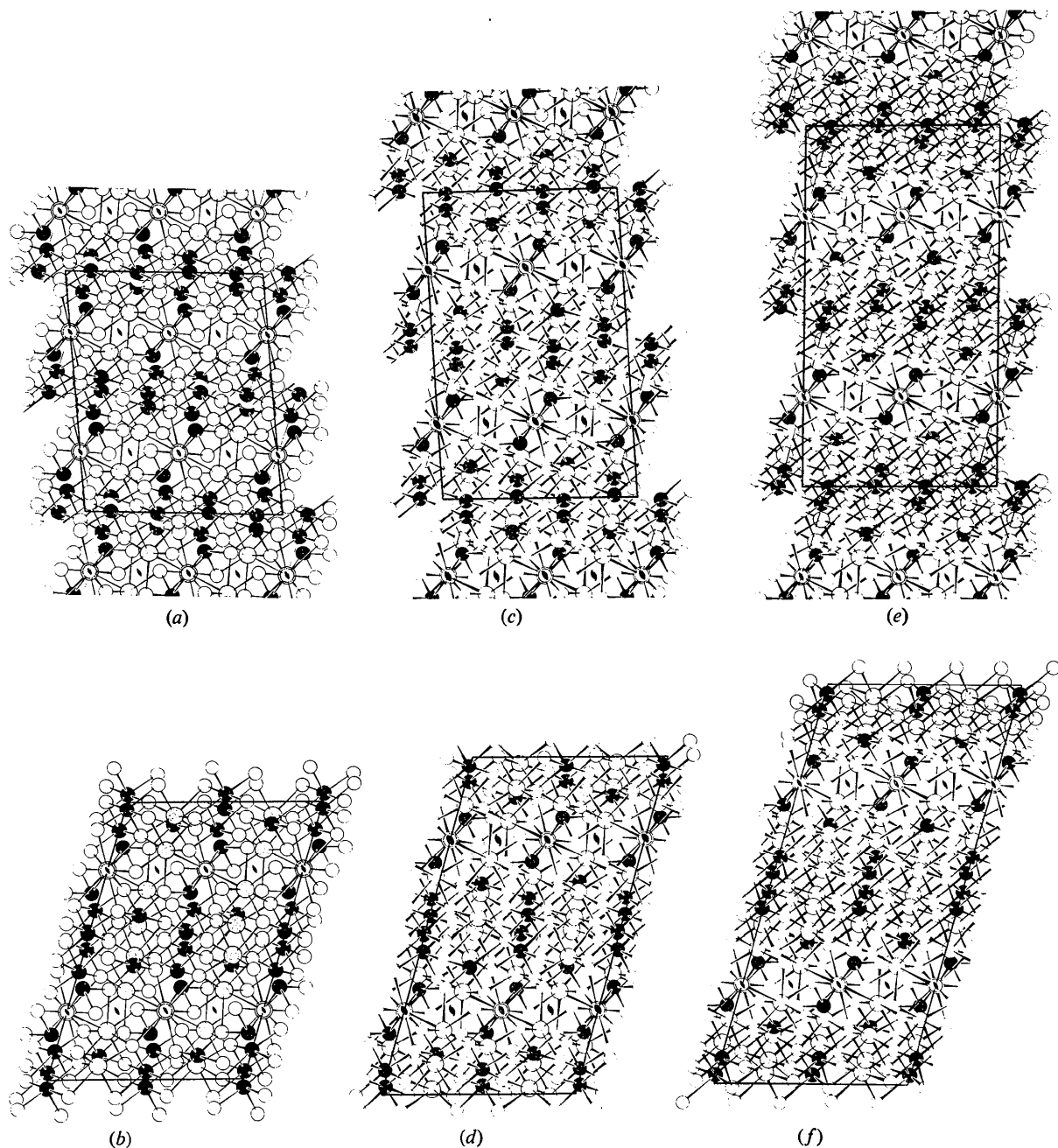

Fig. 1. Projections along **b** of the structures of the plagionite group. (a) Predicted structure for fülöppite, (b) the structure of plagionite, (c) predicted structure for heteromorphite, (d) the structure of semseyite, (e, f) predicted structures for hypothetical phases with $n=4$ and $n=5$. (Shaded circles represent Pb, solid circles Sb, and open circles S atoms.)

References

CHO, S.-A. & WUENSCH, B. J. (1970). *Nature, Lond.* 225, 444–445.

CHO, S.-A. & WUENSCH, B. J. (1974). *Z. Kristallogr.* 139. In the press.

JAMBOR, J. L. (1969). *Miner. Mag.* 37, 442–446.

KOHATSU, J. J. (1973). Ph.D. Thesis, Department of Metallurgy and Materials Science, Massachusetts Institute of Technology.

KOHATSU, J. J. & WUENSCH, B. J. (1974). *Program and Abstracts, Spring Meeting, Amer. Cryst. Assoc.,* Berkeley, California, p. 40.

MEIER, W. M. & VILLIGER, H. (1969). *Z. Kristallogr.* 129, 411–423.

NUFFIELD, E. W. (1946). *Univ. Toronto Studies, Geol. Ser.* 50, 49–62.

Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the Executive Secretary of the International Union of Crystallography (J. N. King, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England).

Molecular Structures and Dimensions

Volume 5 of this series: *Bibliography* 1972–1973, *Organic and Organometallic Crystal Structures,* was published recently by the International Union of Crystallography and the Cambridge Crystallographic Data Centre. This volume contains information on approximately 2000 structures published during 1972–1973. Entries are arranged in 86 chemical classes and cover organic compounds, complexes, and organometallic compounds. There are three indexes: author, formula and transition metal. All are cumulative for the years 1935–1973 and give references to Volumes 1–5. Volume 6 for 1973–1974 is in preparation and is due to appear early in 1975. A new numerical data volume for the years 1966–1969, to follow Volume A1, *Interatomic Distances* 1960–1965, which was published last year, is also in preparation.

The price of Volume 5 has been maintained at the same level as that of Volume 4 and is 55 Netherlands guilders (U.S. \$21.00 or £9·00). Personal copies may be obtained at a reduced price of 39 Netherlands guilders (U.S. \$15.00 or £6·50). The new volume can be obtained direct from Oosthoek, Scheltema & Holkema, Emmalaan 27, Postbus 13079, Utrecht, The Netherlands. Alternatively orders may be placed with Polycrystal Book Service, P.O. Box 11567, Pittsburgh, Pennsylvania 15238, U.S.A., or with the Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, England, or with any bookseller. Standing orders can be placed for the series with Messrs Oosthoek, Scheltema & Holkema to ensure the earliest possible despatch of new volumes as soon as they are published.

Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (M. M. Woolfson, Physics Department, University of York, Heslington, York YO1 5DD, England). As far as practicable books will be reviewed in a country different from that of publication.

High Temperature Crystal Chemistry, Специальная перепечатка из *American Mineralogist* (1973). **58,** 577–704. Страниц 128, Рис. 68, Таблиц 89. Вашингтон : The Mineralogical Society of America, 1973. Цена \$3.50.

Минералогическое общество США сделало весьма полезное дело, опубликовав в 1973 году в *American Mineralogist,* т. 58, труды по высокотемпературной кристаллохимии, доложенные на сессии Американского Геофизического Союза в апреле 1972 г. и на IX Международном конгрессе кристаллографов в августе того же года. Одиннадцать докладов, кроме того, изданы в виде отдельного, ниже реферируемого тома.

Он включает краткое предисловие редакторов и статьи, посвященные исследованиям структур форстерита, гортонолита, акмита, диопсида, геденбергита, жадеита, сподумена, юриита, моноклинных пироксенов из лунного базальта, ромбических пироксенов, тремолита, анортита, натролита, β-эвкриптита при высоких температурах, статью, посвященную уточнению структуры кубического борацита и работу, в которой дается описание сравнительно просто устроенного нового нагревателя кристаллов для прецизионной камеры и четырехкружного дифрактометра, которые хорошо себя зарекомендовали при высокотемпературном исследовании земных и лунных минералов.

Все статьи содержат новый ценный фактический