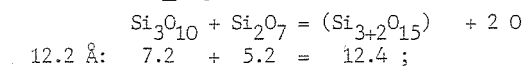


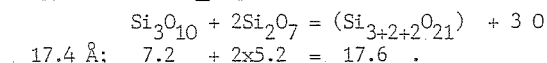
08.1-05 CRYSTAL CHEMISTRY OF Ca, R.E., AND Zr SILICATES, AS DERIVATIVES OF WOLLASTONITE CHAINS. By M. J. Chiragov, Department of Geology, The Azerbaijan State University, 370122 Baku, USSR.

Holmium silicate, $K_2H_2HoSi_3O_{10}$ (Chiragov (1979), Azerb. Univ. Geol. Bull.), is isostructural with $K_3YSi_3O_8(OH)_2$ (Ilyukin (1968), Dokl. Akad. Nauk USSR). Both are inosilicates and the Si_3O_{10} or $Si_3O_8(OH)_2$ groups that are part of their structures can be considered analogous to corresponding groups in the wollastonite chain, from the points of view of symmetry elements, bond angles and oxygen sharing with the cationic octahedron. Similar analogies exist in the arrangement of chains and distribution of cations in the structures of rhodonite $Mn_4CaSi_5O_{15}$ (Mamedov (1958), Dokl. Akad. Nauk Azerb. SSR), babingtonite $Fe^{+3}Fe^{+2}Ca_2Si_5O_{14}(OH)$, inesite $Mn_7Ca_2Si_{10}O_{28}(OH)_2 \cdot 5H_2O$, and pyroxmangite $Mn_3Fe_3CaSi_7O_{21}$. In these silicates the inosilicate groups bond themselves only to the octahedron of the Ca atom. Taking this peculiarity into account, the formation of chain types can be presented as follows:

in rhodonite, c equals



in pyroxmangite, c equals



Our conclusion is that, in silicate structures characterized by derivatives of the wollastonite chain, the basic motifs are the inosilicate groups Si_3O_{10} polymerized with octahedrons of large cations. We consider the scheme of formation of different structural types from simple structural units from this point of view.

08.1-06 CRYSTAL STRUCTURE PREDICTION BY ENERGY MINIMISATION. By C.R.A. Callow, A.N. Cormack, University College London, and F. Theobald, Laboratoire de Chimie Physique, Besançon, France.

This paper will show that calculations of crystal energetics for ionic solids coupled with efficient minimisation routines are capable of predicting the structure of complex inorganic solids, thereby promising to provide a valuable guide in structure refinements. The calculations we discuss are based on exact summations of both Coulomb and short-range components of the lattice energy. Energy minimisation may be performed with respect to all structural parameters. We illustrate the power of our method with two examples. The first concerns the recently discovered 'B' phases of VO_2 and TiO_2 (Marchand et al., Mat. Res. Bull. 15, 1129 (1980)). Energy minimisations were performed starting from an ideal model based on regular octahedra. The minimised structure shows distortions close to those observed in the X-ray refined model for VO_2 . A predicted structure for the analogous 'B' phase of TiO_2 is also presented; no experimental structure is yet available for this phase. Our second example is the mineral forsterite (Mg_2SiO_4) where again we show that distortions from idealised models are correctly predicted. We conclude with a discussion of potential future application of the technique to complex transition metal compounds and to minerals.

08.1-07 STRUCTURE BUILDING PRINCIPLES IN THE Pb-Bi-(Ag,Cu) SULPHOSALTS AND RELATED COMPOUNDS. By Emil Makovicky, Mineralog. Inst., Copenhagen, Denmark.

In comparison with As and Sb, (1) bismuth displays the smallest differences in the lengths of distinct categories of Bi-S bonds (resp. distances) and sometimes forms regular coordination octahedra; (2) the S-S dimensions of the full Bi-S coordination polyhedra differ least from those of the Pb-S polyhedra. In some sulphosalts differences between Pb and Bi are important and they are ordered (cosalite) whereas some are based on, or tolerate extensive mutual Pb-Bi substitution (lillianite, hegyptite, $PbBi_4S_7$, cannizzarite). Introduction of Se for part of S augments the geometrical tolerance for Pb-Bi variations over structural sites and the gamut of structure types. Structurally related compounds will also be quoted.

The structures of the Pb-Bi sulphosalts can be represented as modulated structures, usually based on somewhat deformed "galena-like" structure sliced in different crystallographic directions (slices parallel to (100) of PbS will be called T layers, those parallel to (111) of PbS will be called H layers). The combinations of several modulation operators create distinct structural types; the homologues in each series differ in the H/T match and/or layer thickness: (1) The cannizzarite homologous series with the structures composed of regularly alternating layers H and T which in one direction match after the vernier principle. (2) The galenobismutite homologues with the H and T layers broken into variably long strips by composition non-conservative glide planes. On the latter, zig-zag layers of additional atoms occur. Galenobismutite ($\approx CaFe_2O_4$), weibullite; a modified type: nuffieldite. (3) The cosalite homologous series with zig-zag layers of "galena-like" structure with H- and T- like portions alternating. The

T and H portions of adjacent layers face each other in a non-commensurate match; the composition-conservative glide planes run through the breakpoints of the layers. Cosalite, $Pb_4In_9S_{17}$, a modified type: $Ce_{1.25}Bi_{3.75}S_8$. (4) The lillianite homologous series based on chemical twinning of "galena-like" slabs parallel to (131) of PbS. Trigonal prisms of Pb are inserted in composition planes. The adjacent slabs may be of equal or unequal thickness. Examples: lillianite, heyrovskyite, several Pb-Bi-Ag sulphosalts. (5) The pavonite homologous series similar to (4) but one set of slabs is only 1 octahedron thick and the composition planes are asymmetrically occupied by Bi in square-pyramidal coordination. $\sim PbBi_4S_7$; other homologues are Cu-Bi and Ag-Bi sulphosalts, some with substantial Pb substitution; pavonite, benjaminite. Intergrowth of (4) and (5) is represented by the V-2 and V-3 phases. (6) Layered structures with crystallographic shear. This family consists of non-commensurate alternating H and T layers of various thickness, regularly offset by composition non-conservative shear planes nearly perpendicular to them. Junoite, $Pb_{3\frac{1}{3}}In_6\frac{2}{3}S_{13}$, proudite, nordströmite, $Bi_3In_5S_{12}$. (7) The bismuthinite-aikinite series of derivative structures.

Multiple relationships between the above series exist. The non-commensurability principle is important for (2), (3), (6) making them "broken-up" derivatives of (1). (5) and (4) can also be interpreted using the principles active in (6); (7) using the principles active in (3). Galenobismutite and (5) are special, contracted-set versions of chemical twinning. In the $2\bar{A}$ -shear derivatives of the above types, the pseudooctahedral coordinations of Bi are replaced by square-pyramidal ones, with long remaining Sb(Bi)-S distances, e.g. jamesonite vs. (3), $HgBi_2S_4$ or livingstonite vs. (5), bournonite vs. (7). References will be quoted on the poster.

08.1-08 SERIES OF NONHOMOGENEOUS LINEAR STRUCTURES. By Yu.N.Hryn', Ya.P.Yarmolyuk, E.I.Hladyshevsky. Chair of inorganic chemistry, Lvov State University, Lvov, USSR.

We name the nonhomogeneous linear those structure types, which one can describe by means of a sequence of certain compositionally and coordinationally different "two-dimensional" structure fragments taking turns along a certain axis (named the layering axis). The present paper deals with structure types of tetragonal and orthorhombic symmetry, formed by $BaAl_4$, CaF_2 , AlB_2 , $AuCu_3$, Cu, α -Fe, α -Po fragments. The structure types, consisting of two or three fragments pointed above, form the series describe by parent-structures formulas or by unit cell composition. We propose the numerical symbols, in terms of which one can describe the nonhomogeneous linear structure types. The main differences between our symbols and well known Zhdanov symbols used for homogeneous linear structures is that each numerical, indicating the number of identical fragments placed one after another in the structure, must have two labels: superscript index

indicating its own fragmental symmetry and the subscript one indicating the parent-structure from which this fragment was taken. The numerical symbol describes exactly the sequence of fragments in the structure and gives information about its symmetry.

The structures consisting of fragments mentioned above belong to 22 tetragonal and orthorhombic space groups. Symmetry of over 40 structure types of intermetallic compounds always belongs to one of the 22 space groups (with exception of the cases of deformation and superstructure formation). The real structure types belongs, as a rule, to the most symmetrical groups and have the simplest numerical symbols. Our method of interpretation is useful not only for systematisation and description of the known structure types, but may be used as an instrument for determination of unknown ones. There is a simple linear dependence between the unit cell and fragmental lattice constants, moreover the coefficients in such linear equations are the numerals from the numerical symbols.

08.1-09 REGULARITIES IN BINARY INTERMETALLIC COMPOUNDS. By P.Villars, K.Girgis Institut für Kristallographie und Petrographie CH 8092 Zürich, Switzerland.

Examination of all the 105 known binary structure types containing more than 5 representants* showed that 85% exhibited the following three regularities.

1. A linear $d_{AB} - \bar{R}$ dependence**.
2. A narrow spacefilling, c/a and b/a range for the given structure type.
- 3i. A dependence between the position of the elements in the periodic table and their equipoint occupation in the structure.
- 3ii The existence of a narrow grouping, for represent. of a given structure type, in an isostoichiometric diagram of binary element-combinations.

This diagram (3ii) has been used to put forward one or two possible structure types, with a high probability of existence, for synthesised binary intermetallic compounds. For example, up until 1970 there were 811 known intermetallic compounds with no assigned structure types, and during the past ten years, the structure types of 120 have been established. By using the above diagram, the correct structure type has been proposed for 110 of these.

Footnotes: * W.B.Pearson, Handbook of Lattice spacings and structures of metals, 1967, Pergamon Press.

** d_{AB} is the shortest distance between the elements A and B. This distance depends upon all the lattice constants and position parameters. $\bar{R} = (nR_A + mR_B)/(n+m)$; R_A, R_B are the radii of the elements A and B (E.Teatum et al., LA 2345, June(1960)), n, m are the stoichiometric proportions.