

08.1-13 FACTORS WHICH INFLUENCE THE STRUCTURE OF INTERMETALLIC COMPOUNDS. By K. Girgis, Inst. f. Krist. u. Petrgr. ETHZ, Zürich, Switzerland.

#### 1. Thermodynamic Factors:

Rajasekharan & Girgis (Phys. Rev. (1983) B27, 909) show that, notwithstanding the isotropic nature of Miedema's semiempirical theory for the heat of formation  $\Delta H$  of intermetallic compounds, and contrary to the present view in literature, the parameters  $\Phi^*$ ,  $n_{WS}$  used to predict the sign of  $\Delta H$ , can contribute quantitatively to our understanding of structural phenomena. We found that the structure of an intermetallic compound is dependent on its heat of formation. A clear separation on a map using these two factors is achieved between  $MgCu_2$  and  $SiCr_3$  structure types. The total exclusion of  $SiCr_3$ -type phases from the 250 binary systems in which Laves phases occur and that of Laves phases from the 87 binary systems with  $SiCr_3$ -type phases will be represented. Different examples will be shown.

#### 2. Geometrical Factors:

##### 2.1. Atomic radii and atomic volumes

The interatomic distance,  $d_{AB}$ , designates the shortest distance between atom A and atom B, which depends on all lattice constants. The concentration weighted mean atomic radius,  $R$ , is equal to  $(m.R_A + n.R_B)/(m+n)$  for the compound  $A_m B_n$ , where one takes always  $m \leq n$ . Very high correlation factors have been found, e.g., 37 structure types exhibit correlation factors in the range 0.99 to 1.00.

A similar correlation has been found between the volume of the unit cell  $V_{uc}$ , and the concentration

weighted mean atomic volume,  $\bar{V}$ , which is defined by  $\bar{V} = (m.V_A + n.V_B)/(m+n)$  for an  $A_m B_n$  compound where  $V_A$  and  $V_B$  are the atomic volumes of elements A and B respectively.

##### 2.2. Space Filling Factor:

The ratios  $c/a$ ,  $b/a$  and the generalized space filling factor are found to be in narrow ranges for all representatives of a structure type. In certain cases of pronounced scatter of axial ratios, the structure family may be subdivided. The space filling range for  $Si_3W_5$  type is 0.75 to 0.76. The mean space filling of 700 compounds of different structure types is  $0.74 \pm 0.04$ ; (0.74 for ccp or hcp). This demonstrates the close packing in the structure of intermetallic compounds. (Villars & Girgis, Z. Metallk. (1982) 73, 455).

#### 3. Electron Configuration:

There is a correlation between the position of an element in the periodic table (s-, p-, d-, f-element) and its equipoint position in the structure; e.g. in the case of  $Si_3W_5$  type (I4/mmm) the point positions 4a and 8h are occupied by the p-elements, while the 4b and 16k are occupied by d- or f-elements. The ratio of p- to d-(f-) elements is always 3:5 and never 5:3.

#### 4. Electronegativity:

It has been found that the electronegativity difference in intermetallic compounds is smaller than 0.8. Examples showing this effect in correlation with other factors will be represented.

08.1-14 SYMMETRY GROUPS IN STRUCTURE TYPE ASSIGNMENT AND CLASSIFICATION. By M. O. Figueiredo, Centro de Cristalografia e Mineralogia, I.I.C.T., Alameda Afonso Henriques, 41 - 4<sup>a</sup> E, 1000 Lisboa, Portugal.

Any crystal structure must conform with one of the 230 three-dimensional, three-periodic space groups, which will characterize its real, crystallographic symmetry. However, space-group symmetry alone is not enough to discriminate the crystal-structure type (STP). Further improvements in STP assignment and classification should be attained by considering i) non-crystallographic symmetry operations, ii) coloured symmetry groups, and iii) symmetry groups with continuous dimensions ( $G_n^t$ , where  $t$  stands for the translations, or dimensions remaining periodic, in a  $n$ -dimensional space). The geometry and dimensionality of the structural units (Lima-de-Faria & Figueiredo, J. Solid St. Chem. (1976) 16, 7) could be appropriately specified, and important structural processes - like the condensation of groups, chains, sheets and frameworks out of the corresponding isopoint (same space group) atomic arrays, and the polymerization of groups into chains and/or sheets up to frameworks - would become apparent. As illustrative examples, two low-symmetry space groups ( $C2/m$  and  $C2/c$ ) are examined in connection with four representative types of silicate structures: pyroxenes/amphiboles, micas and feldspars/coesite.

08.1-15 POLYMERIZATION OF ANIONS IN ANHYDROUS BORATES. N.I. Leonyuk, Department of Geology, Moscow State University, Moscow, USSR.

Polyborates account for over 35% of all the anhydrous borates studied structurally. More than 50 varieties of polyanions are known. In polyanions,  $BO_3$ -triangles and  $BO_4$ -tetrahedra form relatively compact groupings that take, usually, the shape of single and double rings. Polymerization trends characterized by the  $n_B/n_O$  ratio have been analysed depending on the value of  $N = N_{M_x O_y} : N_{B_2 O_3}$ , the size of M-cation and its charge. With decreasing N-criterion, the  $n_B/n_O$  ratio increases and anions get more polymerized: isolated  $BO_3$ - and  $BO_4$ -anions are replaced with pyrogroups, then with chain- or circular-type polyanions and, ultimately, with laminar and framework ones. As the N-factor goes down, the share of  $BO_4$ -tetrahedra at first grows and then diminishes. More often their maximum number equal to that of triangles is recorded when  $N=1/2$ . Larger size of cations contributes to the polymerization as well, if less noticeably. On the other hand, growth of their charges brings about a countereffect. Similarly to crystals, melts and glasses are also characterized by more intensive polymerization as  $B_2 O_3$  concentration rises. As polymerization intensities and the number of "free" bonds are, therefore, reduced, the interaction between the anionic motives and cations becomes weaker.